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MONOLAYER FILMS PREPARED BY THE SPONTANEOUS SELF-ASSEMBLY OF SYMMETRICAL AND UNSYMMETRICAL DIALKYL SULFIDES FROM SOLUTION ONTO GOLD SUBSTRATES: STRUCTURE, PROPERTIES, AND REACTIVITY OF CONSTITUENT FUNCTIONAL GROUPS

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Exposure of evaporated gold films supported on silicon wafers to solutions of dialkyl sulfides $(R(CH_2)_m\text{-}S\text{-}(CH_2)_n\text{-}R'$; R and R' = CH_3 or CO_2H) or alkyl thiols $(R(CH_2)_nSH$, R = CO_2H or CH_3) in methanol or ethanol results in rapid formation of a monolayer of the organosulfur compound adsorbed onto the gold. The resulting films have been characterized using a number of techniques, including X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IRS), ellipsometry, and wetting. These self-assembled, supported organic monolayer films are systems that can be used to study problems in the physical-organic chemistry and materials science of organic surfaces, especially the relation between the molecular-level structure of the film constituents and the macroscopic properties of the assembled monolayers. The films are relatively robust: examples formed from both dialkyl sulfides and alkyl thiols withstand

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washing and prolonged soaking in neutral water, but films containing dialkyl
sulfides are destroyed by contact with aqueous base at pH 8-13.   Studies of the
thickness of the dialkyl sulfide films by ellipsometry, of the orientation of
the hydrocarbon chains in these films by IRS, and of the polarity of the
interface between the films and water by contact angle suggest a physical model
for the film of a relatively disordered organic liquid, liquid crystal, or
glass pinned to the gold surface by gold-sulfur coordinative bonds.
Corresponding studies of thiol films suggest that they are more ordered than
the dialkyl sulfide films.   If polar organic functional groups are incorporated
into the terminal positions of the alkyl moieties of the dialkyl sulfide group,
these moieties are presented at the gold-air (water) interface.   Certain
spectroscopic characteristics of monolayer films containing carboxylic acid
groups are anomalous: in particular, on certain films, it was not possible to
detect the carbonyl stretch of the carboxylic acid group by IRS, even though
these films appeared disordered and were confirmed by XPS to contain carboxylic
acid groups.   Examination of variations in the surface polarity of monolayer
films with the structure of unsymmetrical dialkyl sulfides having one methyl-
terminated and one carboxylic acid-terminated alkyl chain suggests that an
excess of only approximately five methylene units in the methyl-terminated
chain is sufficient to provide a film in which the carboxylic acid groups on
the shorter chain are completely hidden from contacting water, insofar as they
have essentially no influence on contact angle (deionized H_2O, pH - 5.6).   The
inference from these studies that water is dominated by very short-range
interactions (<5 Å) confirms similar conclusions from other types of studies.

Monolayer Films Prepared by the Spontaneous Self-Assembly of Symmetrical and Unsymmetrical Dialkyl Sulfides from Solution onto Gold Substrates: Structure, Properties, and Reactivity of Constituent Functional Groups[1]

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Abstract. Exposure of evaporated gold films supported on silicon wafers to solutions of dialkyl sulfides ($R(CH_2)_m-S-(CH_2)_n-R'$; R and $R' = CH_3$ or CO_2H) or alkyl thiols ($R(CH_2)_nSH$, $R = CO_2H$ or CH_3) in methanol or ethanol results in rapid formation of a monolayer of the organosulfur compound adsorbed onto the gold. The resulting

films have been characterized using a number of techniques, including X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IRS), ellipsometry, and wetting. These self-assembled, supported organic monolayer films are systems that can be used to study problems in the physical-organic chemistry and materials science of organic surfaces, especially the relation between the molecular-level structure of the film constituents and the macroscopic properties of the assembled monolayers. The films are relatively robust: examples formed from both dialkyl sulfides and alkyl thiols withstand washing and prolonged soaking in neutral water, but films containing dialkyl sulfides are destroyed by contact with aqueous base at pH 8-13. Studies of the thickness of the dialkyl sulfide films by ellipsometry, of the orientation of the hydrocarbon chains in these films by IRS, and of the polarity of the interface between the films and water by contact angle suggest a physical model for the film of a relatively disordered organic liquid, liquid crystal, or glass pinned to the gold surface by gold-sulfur coordinative bonds. Corresponding studies of thiol films suggest that they are more ordered than the dialkyl sulfide films. If polar organic functional groups are incorporated into the terminal positions of the alkyl moieties of the dialkyl sulfide group, these moieties are presented at the gold-air (water) interface. Certain spectroscopic characteristics of monolayer films containing carboxylic acid groups are anomalous: in particular, on certain films, it was not possible to detect the carbonyl stretch of the carboxylic acid group by IRS, even though

these films appeared disordered and were confirmed by XPS to contain carboxylic acid groups. Examination of variations in the surface polarity of monolayer films with the structure of unsymmetrical dialkyl sulfides having one methyl-terminated and one carboxylic acid-terminated alkyl chain suggests that an excess of only approximately five methylene units in the methyl-terminated chain is sufficient to provide a film in which the carboxylic acid groups on the shorter chain are completely hidden from contacting water, insofar as they have essentially no influence on contact angle (deionized H_2O, pH = 5.6). The inference from these studies that wetting is dominated by very short-range interactions (<5 Å) confirms similiar conclusions from other types of studies.

Introduction

This paper describes the preparation of organic monolayer films by adsorption of dialkyl sulfides from alcohol solution onto supported evaporated gold films and examines relations between the molecular structure of the adsorbed dialkyl sulfides and macroscopic properties of the films. The broad objective of the program of which this work is a part is to develop methods for preparing organic thin films and interfaces with atomic-level control over interfacial structure, in order to explore phenomena such as wetting,[3] adhesion,[4] biocompatibility,[5] corrosion,[6] and lubrication.[7] The specific objectives of the work reported in this paper are to infer the stability and structural order of monolayer films based on dialkyl sulfides adsorbed on gold using both

spectroscopic techniques and wettability as probes, and to test strategies for assembling monolayer films having macroscopic surface properties (especially wettability) defined by the molecular structures of their components.

Organic compounds containing sulfur adsorb strongly onto gold and other metals and form monolayers.[8-11] These "self-assembled" monolayers have a number of advantages as substrates for the study of organic surface chemistry. They are more easily prepared than Langmuir-Blodgett films, and are certainly no more difficult to characterize.[12] They are intrinsically simpler structurally than the interfacial region of surface-functionalized polymers,[13-16] since their thickness is fixed at one molecular layer. They are usually more stable than organic crystals and more easily obtained with large areas of surface. Infrared spectroscopic and electrochemical studies have indicated that both alkyl thiols and dialkyl disulfides form monolayers that are highly ordered.[10] Similiar claims have been made for monolayer films based on long-chain alkyl silanes covalently attached to glass[17] and silica,[18] and fatty acids adsorbed on oxidized aluminum[19] and silver[20,21] but the interpretation of the spectroscopic evidence in terms of interfacial structure remains controversial. Detailed studies of interfacial properties as a function of systematic variations in the structure of a single adsorbate system have remained an obvious need to increase the understanding of organic interfaces.

Systems based on dialkyl sulfides are, in principle, partic-

ularly attractive as the basis for studies of structure-property

relationships since the structures of the two alkyl groups

connected to sulfur can be varied independently by straightforward

synthetic methods: this variation permits a degree of control of

the local structure of the adsorbed monolayer that is not easily

possible with other organosulfur compounds, or, broadly, with

monolayer films prepared by assembly of components based on simple

fatty acid derivatives. The particular hypothesis used as the

basis for this work is summarized in Figure 1. Adsorption of an

unsymmetrical dialkyl sulfide, $CH_3(CH_2)_nS(CH_2)_mCO_2H$, through sulfur

onto a gold surface results in a monolayer film whose structure

depends both on the molecular composition of the dialkyl sulfide

and on the details of its packing and ordering. The two chains of

these types of dialkyl sulfides terminate in groups having

different hydrophilicity and polarity--methyl and carboxylic acid.

If the films are structurally ordered in a way that places the

polymethylene chains roughly perpendicular to the surface of the

metal, and if the length of the carboxylic acid-terminated chain is

equal to that of the methyl-terminated chain, we expect the polar

carboxylic acid to be exposed at the film-water interface and to

influence wetting. If the methyl-terminated chain is longer than

the carboxylic acid-terminated chain, we expect the interface

between the organic film and a wetting liquid to be CH_3/CH_2-like

(that is, non-polar in character).

If the adsorbed film is structurally disordered and

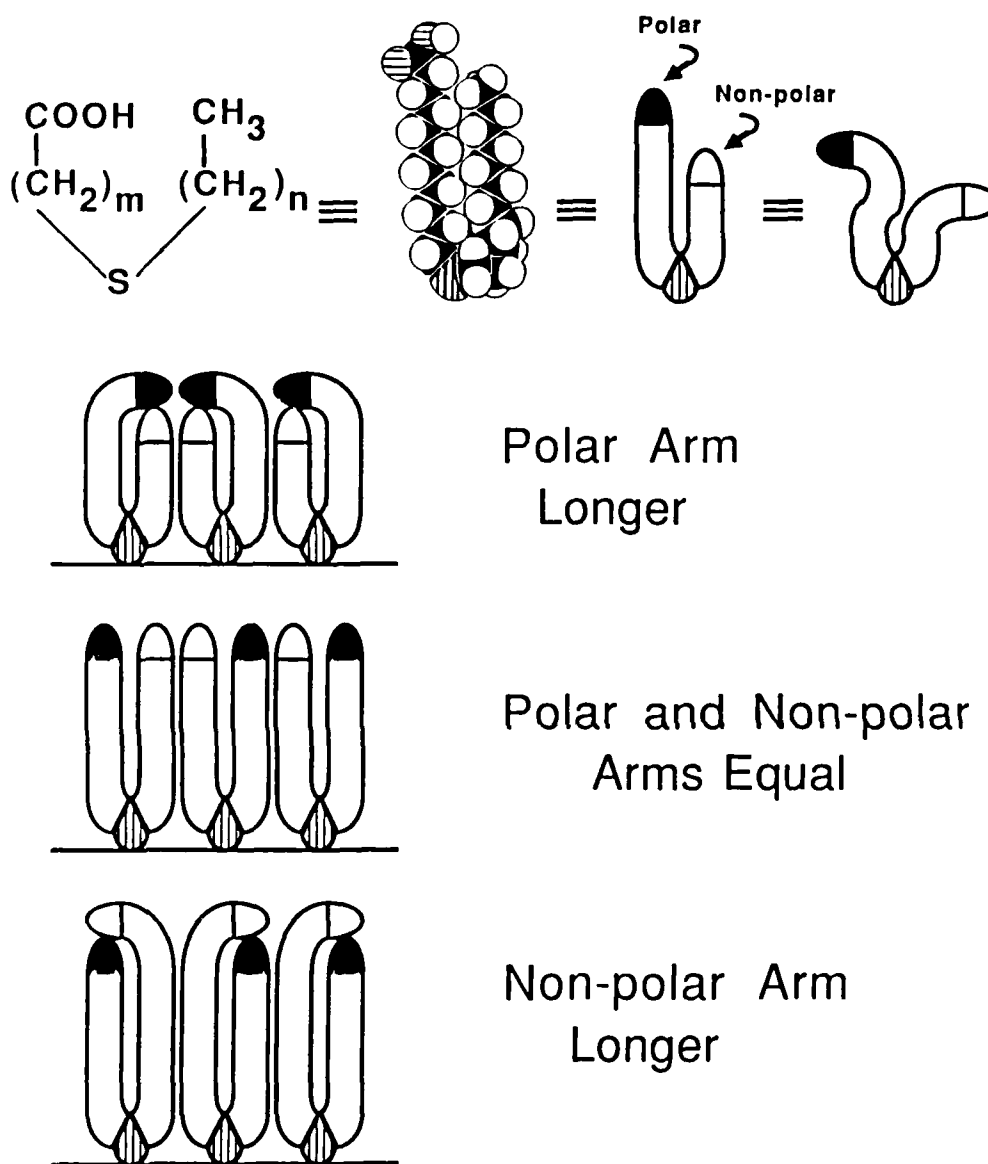liquid-like, we cannot predict its wettability a priori, but expect

Figure 1. Schematic illustration of the physical-organic approach
to the design of interfaces with "buried"
functionality. The alkyl chains are indicated here as
extended only for illustration; they are almost
certainly less ordered than these diagrams suggest.

to be able to infer at least certain of its structural characteristics from comparisons of wettability and spectroscopic character with those of better-characterized model systems. Thus, by systematic variation in the structures of dialkyl sulfides adsorbed on gold, we expect to be able to determine many features of the structures of these monolayer films. In the event that the film is highly ordered, we would have available an extremely flexible system with which to study the properties of interfaces between liquids and organic solids; in the event that the film is less well ordered, this system might still prove valuable in studying organic surface chemistry.

This work relies on a number of conventional optical and spectroscopic techniques to characterize the adsorbed film, but places particular emphasis on measurements of wettability. The reason for this emphasis is the inference from our work[13,14] and from that of others[22] that wetting is one of the most "surface sensitive" techniques presently available. Wetting has the further useful characteristic that it is applicable to the study of interfaces between condensed phases--a regime that cannot be explored using many spectroscopic techniques requiring high vacuum--and that it is a technique that is particularly simple experimentally.

Early evidence that the free energy of a solid-liquid interface is influenced only by atoms at or close to that interface came from Langmuir's "Principle of Independent Surface Action"[23,24] and from investigations of the wettability of polymers and

monolayer films carried out by Zisman and others.[25-28] Zisman's studies included a wide variety of substrates, and suggested that solids containing molecules with large uncompensated dipoles could affect wetting properties even if these dipoles were "buried" under the outermost layers of a solid surface.[27] In an important study,[27] Shafrin and Zisman demonstrated that the wettability of monomolecular films of a series of adsorbed acids having the structure $CF_3(CF_2)_n(CH_2)_{16}CO_2H$ (n = 0,1,2,4, and 6) decreased with increasing length of the perfluoroalkyl group up to n = 7; at this point, the film had wetting properties that resembled those of monolayer films prepared from perfluoroctanoic acid. More recent studies have compared surface compositions in reconstructing polymers using XPS and wetting,[13-16] and have measured directly the interaction between solids, including organic films, using film balance techniques.[29]

In none of these studies is interpretation unambiguous, since in none is the structure of the interface unambiguously determined. Nonetheless, two general conclusions emerge: Where van der Waals interactions determine the energy of a solid-liquid interface, the interactions that determine wetting fall off roughly as r^{-6} and are thus very short range in character--probably extending over no more than one to two atomic layers (3-6 Å). Dipole interactions fall off more slowly (r^{-3}) and may in particular systems[27] extend into deeper layers of the solid (10 Å). By contrast, photoelectron spectroscopy--a "surface sensitive" spectroscopy--typically samples 35-100 Å of the surface of non-metallic materials.[30]

In this work, we have used carboxylic acid groups as our polar group of choice in probing the surface for several reasons.[13-16,31,32] First, carboxylic acid groups are hydrophilic and strongly influence wettability. Second, they can be converted into more hydrophilic carboxylate anions by deprotonation, and this deprotonation reaction can be conveniently followed by measuring the contact angle of buffered aqueous solutions (contact angle titration).[13] The acidity inferred for carboxylic acids at interfaces can be compared with the body of information concerning the acidity of carboxylic acid groups in solution. Third, we have used carboxylic acid groups and contact angle titration extensively in examining the properties of surface-modified polyethylene, and have available a large amount of information for comparison.[13-16] Fourth, the behavior of carboxylic acid groups at interfaces is relevant to a wide range of other phenomena in materials science[33,34] and biology.[35-37]

We note explicitly that the concepts of "surface" and "interface" are not uniquely defined for systems of the types examined here, and are probably best described in terms of specific experimental measurements.[15] We will use the word "surface" to indicate that part of a condensed phase in direct van der Waals contact with another phase. This word is reasonably sharply defined in discussing the outermost atomic layer of gold atoms of the substrate and its interactions with coordinated sulfur atoms, but is more difficult to apply to the organic monolayers, particularly if these are disordered, mobile, or swollen by a

contacting liquid.

Results

General Considerations. Organic monolayer films of dialkyl sulfides were prepared by dipping a thin, evaporated gold film supported on a single-crystal silicon wafer into an alcoholic solution of the dialkyl sulfide at room temperature for intervals of time ranging from minutes to hours. The adsorption process, and the characteristics of the resulting films, were followed using a number of techniques, of which ellipsometry, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy and measurement of contact angle using aqueous solutions were the most useful. To obtain reproducible results in these experiments required careful attention to detail at a number of points, most particularly in the preparation and purification of the dialkyl sulfides. We discuss each of these techniques in turn.

Preparation and Handling of Gold Substrates. The gold substrates were prepared by thermal evaporation of a ~2000-Å thick layer of high-purity gold onto chromium-primed, electronic-grade single crystal silicon wafers. During the course of the experimental work, gold films were prepared using five different evaporators, including both thermal and electron-beam sources. Four of these evaporators yielded films that gave rise to monolayer films having similiar properties; the one exception is discussed further in the experimental section. The gold films were not annealed before use: upon annealing in oxygen at 300 $^{\circ}$C, the gold

surface became cloudy and adopted a silvery hue, probably due to migration of chromium and/or silicon to the gold-air interface. After preparation, samples were ordinarily stored in wafer trays wrapped with Parafilm and were not intentionally exposed to contaminants, but were not otherwise protected. They could be stored before use for at least one week without influencing the properties of the film. With minimal handling of the samples, XPS (see below) showed little carbon or sulfur contamination on the gold. It is clear, however, that the surface of the gold was contaminated by adsorbed impurities; the contact angle of water on these samples was typically θ_a ~60° compared to value of θ_a ~0°-8° reported for clean gold.[38-40] Nevertheless, the monolayers prepared by adsorption on this gold had reproducible properties; we believe that the strongly adsorbing organosulfur compounds displaced residual elements of the adventitious contaminating surface film. Ellipsometry was not useful for the determination of the absolute values of the thickness of the contaminants preadsorbed on gold after removal from the evaporator both because of poor reproducibility (at this level of analysis: 5-30 Å) of the optical properties of samples prepared in different evaporations, and due to the absence of a suitable reference value for gold. Gold samples stored in wafer trays or exposed to the laboratory atmosphere for even a few hours rapidly adsorbed contaminants, as indicated by the increase in the water contact angle from 60° to 90°, and the accumulation of a thick film (4-10 Å) by ellipsometry. Before use in the preparation of monolayers, the substrates were

cleaned by brief washing with ethanol. This washing appeared to remove many of the adsorbed contaminants; ellipsometry showed a decrease in the thickness of the adsorbed film and the contact angle decreased from 90° to $55-70^{\circ}$.

The gold surface obtained by evaporation in vacuum, exposure to the laboratory atmosphere, and washing with ethanol, was, thus, a suitable substrate in the sense that any impurities adsorbed on it had minimal effects on the properties of the organic monolayers and on the characterization of these monolayers, but certainly was not "clean" in the sense used in high vacuum physics. In these and other studies of organic surface chemistry[19] we have been surprised by the relative insensitivity of the results to details of the history of the sample. In the case of organosulfur compounds adsorbed on gold, we believe that this insensitivity reflects two circumstances: first, organosulfur compounds coordinate strongly to gold, and displace most organic contaminants present on the gold surface. Independent studies to be reported later[41] indicate that organosulfur compounds exchange between the gold surface and a contacting solution: thus, organosulfur compounds may even displace other organosulfur contaminants. Second, the organic monolayers themselves constitute interfaces having low interfacial free energies and do not adsorb contaminants strongly. It is probable that some of the scatter in our ellipsometric data is due to variable quantities of impurities adsorbed on the gold surface before formation of the monolayer, and perhaps to residual contaminants not displaced by dialkyl sulfides. Ce. .ain problems

in reproducibility with the monolayer systems encountered periodically during this work seem to be correlated with the accidental presence of volatile organic thiols in the laboratory atmosphere due to activities of other workers.

It is difficult to characterize the surface of these gold substrates. Examination of typical substrates by scanning electron microscopy (SEM) shows no distinctive features at a scale of ~1000 Å (Figure 2). Diffraction and cross-sectional TEM studies indicate that these gold films are polycrystalline with an average grain size of the order of 500-1000 Å and exhibit a very strong (111) texture, perhaps exceeding 90% of the total surface.[11] The films are homogeneous and uniformly and sharply reflective to the eye. Present crude theories of wetting[42-45] do not, however, take into account atomic-level surface microheterogeneity, especially in circumstances of the sort encountered with adsorbed thin films (Figure 3). Thus, for example, a step on the gold surface of only a few Ångstroms may expose in a perfectly oriented monolayer of carboxylic acid-terminated dialkyl sulfides methylene groups that would otherwise be hidden in a completely planar surface. If the surface free energy is considered as an area-weighted superposition of contributions from directly exposed organic groups,[13,23,24] roughness at this scale might have a profound influence on the characteristics of the interface.

In practice, we cannot comment on the influence of roughness on the properties of these monolayer films other than to say we have seen no evidence that roughness is important. Samples of
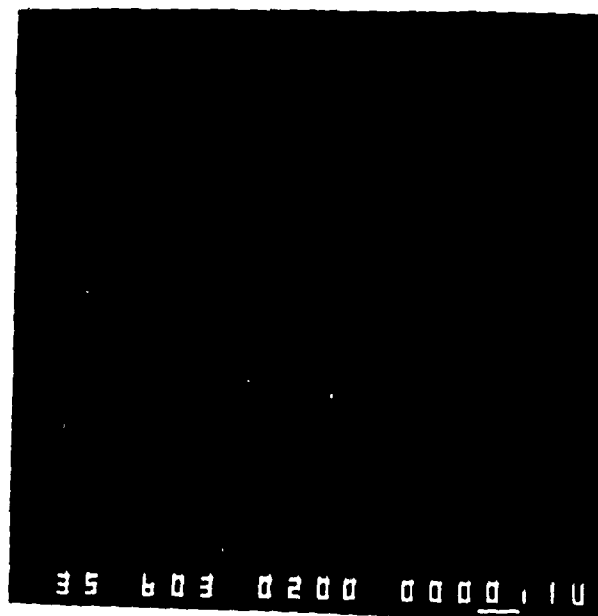
Figure 2.   Scanning electron micrograph of a gold sample
            representative of those used in these studies.   A
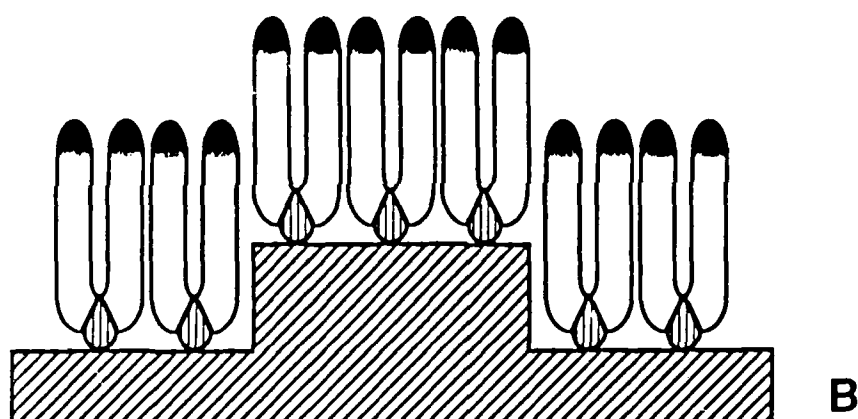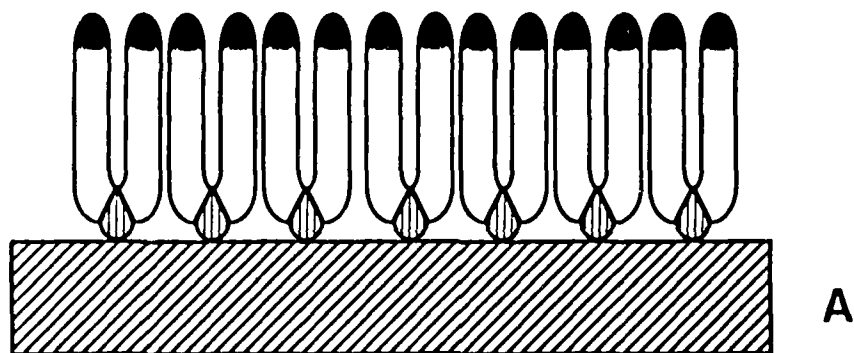   100-nm bar is shown.

Figure 3. Schematic illustration of the influence of a small plateau on the interface presented by $S[(CH_2)_nCO_2H]_2$.
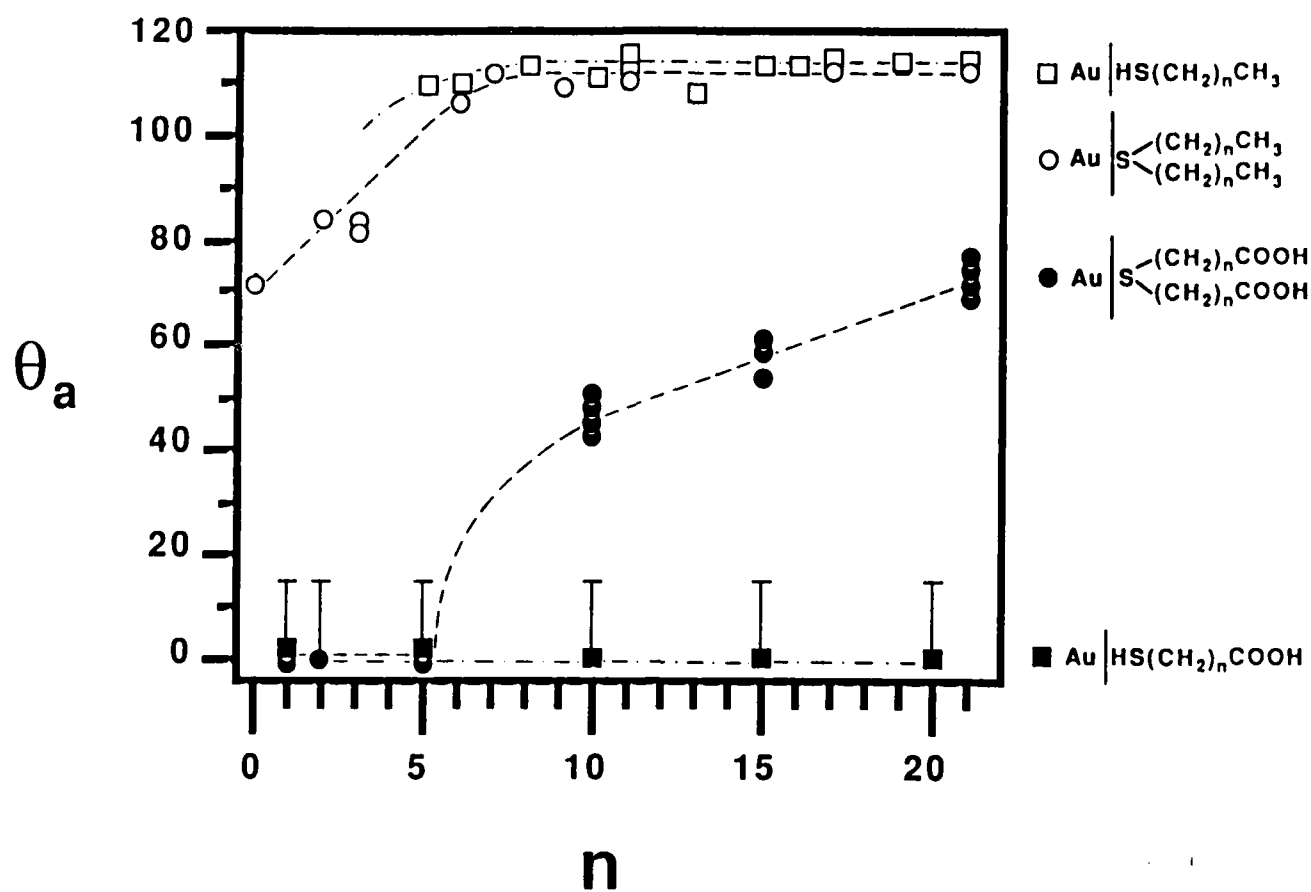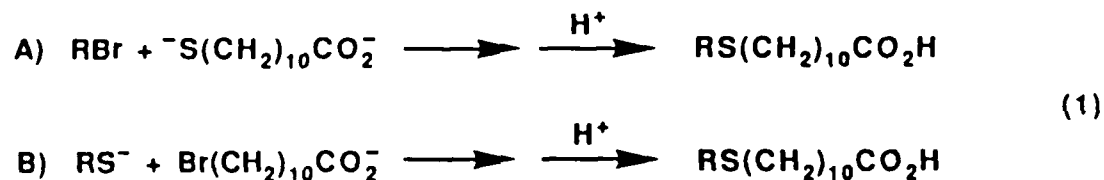
Figure 4. Values of contact angle (deionized water, pH = 5.6) for
representative films as a function of chain length.

supported evaporated gold prepared in different evaporators--systems that almost certainly produce different degrees of microscopic surface roughness--yield organic monolayers showing very similiar macroscopic surface properties.

Preparation of Dialkyl Sulfides. These compounds were prepared by displacement of bromide from alkyl bromides by a thiolate anion (eq 1). It was critically important to purify the

<u>Method</u>

A) $RBr + {}^-S(CH_2)_{10}CO_2^- \xrightarrow{\quad\quad} \xrightarrow{\text{H}^+} RS(CH_2)_{10}CO_2H$

B) $RS^- + Br(CH_2)_{10}CO_2^- \xrightarrow{\quad\quad} \xrightarrow{\text{H}^+} RS(CH_2)_{10}CO_2H$

(1)

dialkyl sulfides to homogeneity and particularly to ensure the absence of thiols as impurities. For many of our experiments, the dialkyl sulfides used as adsorbates were prepared by two independent methods (methods A and B, eq 1), as a check for contaminants introduced during synthesis. Thiol impurities coordinate to gold more strongly than dialkyl sulfides, and concentrate at the interface preferentially. Impure $CH_3(CH_2)_{17}S(CH_2)_{10}CO_2H$, prepared using method A, initially yielded monolayer films having $\theta_a < 10°$, while the same compound prepared using Method B gave $\theta_a = 111°$. Carefully purified samples prepared using either method gave the same result: $\theta_a = 111°$. Intentional doping of this dialkyl sulfide with 1% (w/w) of a thiol demonstrated that, even at these levels, thiol impurities strongly

affect the wettability of the films. For example, doping of impure $CH_3(CH_2)_{17}S(CH_2)_{10}CO_2H$ prepared by method A with 1% $CH_3(CH_2)_{17}SH$ increased the contact angle from $\theta_a < 20^\circ$ to $\theta_a \sim 112^\circ$. Doping of the same sulfide prepared by method B with 1% $HS(CH_2)_{10}CO_2H$ decreased θ_a from 111° to $< 20^\circ$: these contact angles are indicative of almost exclusive incorporation of the thiol into the monolayer. We considered dialkyl sulfides to be pure when they yielded monolayer films whose wettability was independent of the method used for their synthesis.

Preparation of Self-Assembled Monolayer Films by Adsorption of Dialkyl Sulfides from Solution onto Gold.

General Features. The gold substrate was rinsed with methanol or ethanol before use. The dialkyl sulfide was dissolved in the same solvent; other solvents such as THF were less generally useful (either because they left visible precipitates on the surface, or because the solubility of the dialkyl sulfides in them was inconveniently low) but were occasionally used. Dialkyl sulfides of high molecular weight ($n \geq 12$) were not soluble at concentrations of 0.05 M in methanol, ethanol, hexane, or hexadecane. Monolayers prepared from saturated solutions in these solvents had, however, wetting properties that were similiar to those films prepared from tetrahydrofuran solutions (~ 0.005 M) in which the solubility is higher. The gold film was immersed in a solution of the dialkyl sulfide (typically for 12-36 h), removed, washed with a small amount of the same solvent, and dried briefly

in a stream of argon. Some of these systems were not autophobic; they emerged wet from the solution used and required washing to avoid the formation of multilayer films. Unless extended, washing had no important effect on the observed film thickness or wettability. For example, films prepared by adsorption of didocosyl sulfide from tetrahydrofuran solution for 3 h were not affected (ellipsometry, contact angle with water or hexadecane) by ten consecutive cycles of washing with ethanol and drying, or by sonication for 10 min in ethanol (see the Experimental Section).

The stabilities of the monolayer films were, in general, good. They could be stored for extended periods of time in wafer trays or glass vials. Films showing evidence of some contamination (for example, an unexpectedly high value of contact angle with water suggesting adsorption of hydrophobic contaminants) could generally be cleaned by brief washing with 0.1 N HCl, water and ethanol. Exposure to strong base led to irreversible changes in wettability. The monolayers were, however, stable for at least 24 h in water over the pH range 1 to 7. The monolayers prepared from dialkyl sulfides were not stable at high temperatures ($\sim$80 $^{\circ}$C) nor to certain reagents including 30% hydrogen peroxide and ethereal solutions of diborane and phosphorous pentachloride.

Contact Angle. Techniques used to measure the contact angle, θ, have been described in detail elsewhere.[13] All measurements were made at 100% relative humidity. Although, in principle, the pH of the solution used in measuring θ is important in these types of studies,[13] in practice, most measurements were

made using unbuffered, deionized water at pH 5.6. The
insensitivity of most of these samples to pH is discussed in
greater detail below. For pH titrations, the buffers described
previously were employed.[13] The monolayer films were unstable at
values of pH greater than 7. For the sake of consistency, all
measurements of contact angle with drops of pH > 7 were made within
1 min after application of the drop to the surface. The values
reported may not represent true stationary angles. In this work,
as in most of our studies of organic surface chemistry, samples
exhibited significant hysteresis in the measured contact angles,
and we normally report an advancing angle, θ_a, obtained after the
spontaneous advance of the drop edge had stopped. The hysteresis
$\theta_a - \theta_r$, measured in degrees) seemed to correlate more with the
polarity of the sample than with surface roughness: more polar
surfaces (lower values of θ_a) showed larger hysteresis. The
samples used here were flat by the standards of most samples used
in measuring contact angles; it seems unlikely that the observed
hysteresis ($\Delta\theta = \theta_a - \theta_r = 10^\circ$ at $\theta_a = 110^\circ$, $\Delta\cos\theta = \cos\theta_a - \cos$
$\theta_r = -0.17$; $\Delta\theta = 25^\circ$ at $\theta_a = 75^\circ$, $\Delta\cos\theta = -0.30$; $\Delta\theta = 40\text{--}50^\circ$ at
$\theta_a = 50^\circ$, $\Delta\cos\theta = -0.36$) is due either to surface roughness or to
heterogeneity at the micron scale. There are no theories that
currently discuss hysteresis in terms of atomic scale
heterogeneity, and we note that $\Delta\cos\theta$, a measure of the
difference in measured interfacial free energies for advancing and
receding drops, varies relatively little. It is thus unclear
whether the apparent change in hysteresis with polarity is a real

phenomenon, or an artifact of considering $\theta_a - \theta_r$ rather than $\cos \theta_a - \cos \theta_r$. Retreating contact angles, θ_r, show the same general trends as advancing contact angles. Values of $\theta_a < 15^\circ$ are unreliable, and such values are shown on plots as $\sim 0^\circ$.

For reference, Figure 4 plots θ_a as a function of chain length for monolayer films formed from four sets of compounds: dialkyl sulfides terminating in methyl groups and carboxylic acid groups, and alkyl thiols also terminating in these groups. Evidence discussed elsewhere[10,46,47] suggests that alkyl thiols form highly ordered, close-packed monolayers. The contact angle of water on the methyl surface of n-alkyl thiols is among the highest known for smooth surfaces ($\theta_a = 114^\circ$, deionized H_2O, pH = 5.6; for comparison, $\theta_a = 103^\circ$ for polyethylene). Similiarly, the ω-carboxylic acid alkylthiols present very polar surfaces: at all values of pH for these surfaces, we measure $\theta_a \simeq 0^\circ$. This value is much lower than corresponding values for carboxylic acid-terminated dialkyl sulfides. We infer from these comparisons that, for example, the carboxylic acid groups of symmetrical, carboxylic acid-terminated dialkyl sulfides are less tightly packed at the interface than are the carboxylic acid groups of the analogous alkyl thiols. Again, by way of comparison, the value of θ_a observed for an equilibrium monolayer of $S((CH_2)_{15}CO_2H)_2$ is similiar to that observed for a monolayer containing a 1:1 mixture of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$.[41]

Certain other organic monolayer systems, such as those derived from carboxylic acid-terminated alkyl silanes,[48,49] are

similiar in their wetting properties to the carboxylic acid-terminated dialkyl sulfides, but less hydrophilic than carboxylic acid-terminated alkanethiols. We suggest that these silane systems are probably also relatively disordered.

Ellipsometry. Ellipsometry provides a convenient, qualitative, but not necessarily highly accurate method of estimating coverage and film density by measurement of the thickness of the monolayer deposited on the gold substrate. The sorts of systems used here are probably close to ideal for ellipsometry: compounds typically differ primarily in the length of the $(CH_2)_n$ chain.

The ellipsometric procedure used in these systems involves the determination of two sets of polarizer and analyzer readings for each gold substrate and before and after adsorption of a monolayer film. Each set of readings comprises the polarizer and analyzer settings averaged over three or more locations on the sample separated by at least 1 cm, and has a maximum error of $\pm 0.15°$, corresponding to ± 3 Å in the thickness. The effect of substrate roughness on ellipsometric measurements has been discussed elsewhere[19,50] and is not expected to affect significantly measurements on these evaporated gold substrates. Since film thicknesses are calculated from the differences in the optical properties of the "bare" substrates and the substrates coated with monolayers, it was necessary to make some assessment of the possible effects on ellipsometric measurements of contamination of both the substrates and monolayer films, of the use of bulk

values for the index of refraction of the molecular components of these films, and of the relative binding affinities of dialkyl sulfides and contaminants to gold. The uncertainty in the measured film thickness due to contaminants is probably less than 4 Å based on previous studies of gold using ellipsometry by McCrackin[50] and the agreement between film thicknesses determined experimentally and values derived from molecular models. Further, XPS and infrared spectroscopy are consistent with the proposed structures of these films and provide no evidence of gross contamination of either the substrate or the monolayer. The difference in intercepts for the thicknesses (see below) plotted against chain length of carboxylic acid and methyl-terminated thiols, may arise from adsorption of water by the hydrophilic, carboxylic acid surface. The extent of adsorption of water on films of $CH_3(CH_2)_nS(CH_2)_{10}CO_2H$ is unclear. The calculated thickness for these films is insensitive to the index of refraction used. We have assumed a bulk value of $n = 1.45$ of the index of refraction for these films; however, values of thickness are changed only by about 3 Å on varying n from 1.35 to 1.55.

Figure 5 compares the reproducibility of data obtained by ellipsometry and measurement of contact angle. Each set of points represents a series of data obtained on the same sample. That is, each set of points represents independent measurements of contact angle and ellipsometric thickness at approximately the same point on a sample. It is not practical to measure the contact angle and ellipsometric thickness at exactly the same point, but the points
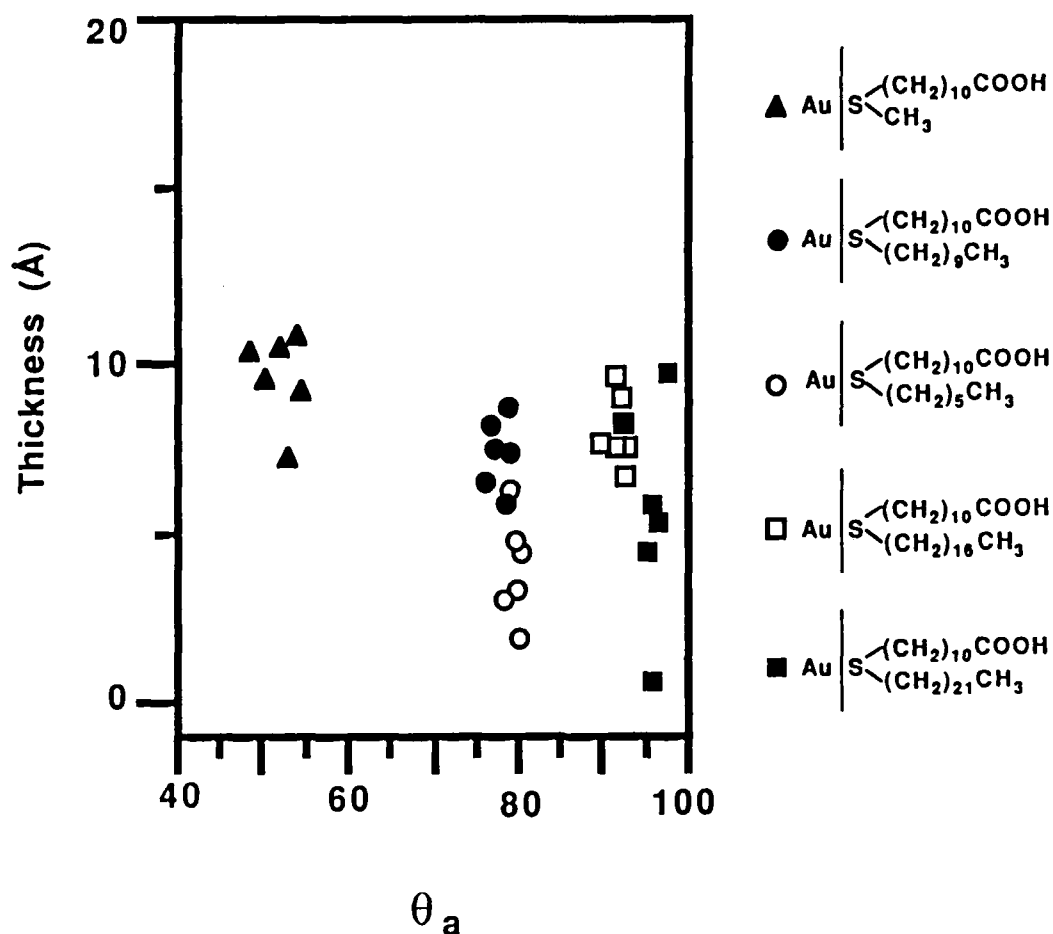
Figure 5.   Measurement of film thickness (by ellipsometry) and contact angle (deionized water, pH = 5.6) for representative films. Values of thickness and contact angle were obtained close to one another, but not necessarily at exactly the same location. All points having the same symbol were obtained using one sample. The data for $CH_3(CH_2)_{21}S(CH_2)_{10}CO_2H$ are representative of data showing an <u>unacceptable</u> level of reproducibility (presumably due to contamination of the surface at some point during the preparation of the film); data for other compounds show scatter that we considered normal and acceptable.

used for each of these measurements were made to correspond as closely as possible. These data lead to two important conclusions. First, the scatter in the data for θ_a is appreciably less than in the ellipsometric thicknesses; small changes in θ_a are more significant than comparable variations in the ellipsometric thickness. Second, there is no correlation between deviations from the mean in thickness and contact angle. Thus, the scatter both in thickness and in contact angle appears to be random, rather than representing, say, real variations in film thickness and wettability from point to point on the sample. The scatter in Figure 5 observed for films of $CH_3(CH_2)_{21}S(CH_2)_{10}CO_2H$ is due to the use of an unsuitable gold substrate for the preparation of this sample and is not representative of films prepared from this compound.

Figure 6 compares the estimated thickness of the adsorbed monolayer as measured using ellipsometry for five homologous sets of compounds: methyl-terminated n-alkyl thiols and symmetrical dialkyl sulfides; carboxylic acid-terminated n-alkyl thiols and dialkyl sulfides; "mixed" unsymmetrical dialkyl sulfides having the form $CH_3(CH_2)_nS(CH_2)_{10}CO_2H$. The estimated thicknesses of methyl-terminated films are very similiar for alkyl thiols and dialkyl sulfides. We believe that the alkyl thiols form highly ordered monolayers;[10,46,47] the inference from this work is that the dialkyl sulfides probably also show a significant degree of order, since the films are of comparable thickness and, hence, of a similiar packing density. The data for carboxylic acid-terminated
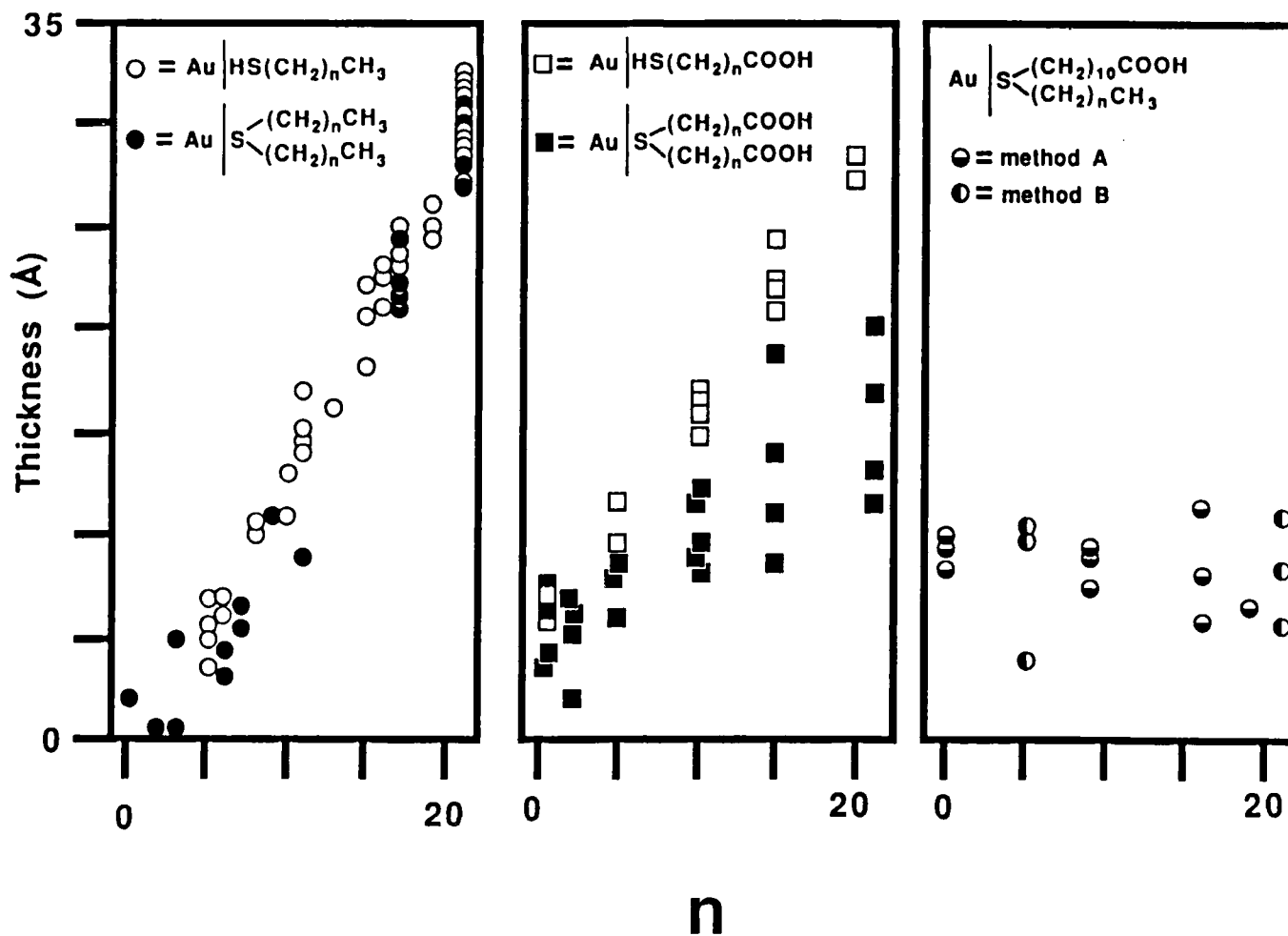
Figure 6.   Film thickness (by ellipsometry) of representative films as a function of chain length.

systems suggest that the carboxylic acid-terminated and methyl-terminated alkyl thiols form monolayers of similiar thickness (and, hence, probably similiar order), while the films formed from symmetrical carboxylic acid-terminated dialkyl sulfides are significantly less thick than those formed from the homologous methyl-terminated dialkyl sulfides. The origin of the difference between carboxylic acid-containing systems and methyl-terminated systems is unclear, but is probably not due solely to hydrogen bonding because preliminary studies indicate that the methyl ester-terminated system resembles the carboxylic acid-terminated system. At this time, our best hypothesis is that the energy required to align the dipoles in the carboxylic acid-terminated system is not compensated by the cohesive van der Waals interactions between chains. As a result, this system is loosely-packed.

Perhaps most puzzling are the data for the unsymmetrical dialkyl sulfides. The ellipsometric data suggest essentially no change in film thickness as the length of the methyl-terminated alkyl group changes from CH_3 to $(CH_2)_{21}CH_3$. It may be possible to rationalize this observation on the basis of disorder in the film and relatively low sensitivity of ellipsometry to small changes in film thickness, but it nonetheless remains surprising. The inference from comparisons of carboxylic acid-terminated symmetrical dialkyl sulfides and carboxylic acid-terminated thiols is that the dialkyl sulfides are more loosely packed, less dense systems. If this difference in density is conserved for the

components of the unsymmetrical dialkyl sulfides, we expect only a
relatively modest increase in measured thickness in changing the
length of the alkyl chain. For example, a monolayer of
$CH_3S(CH_2)_{10}CO_2H$ might be expected to be ~5 Å thinner than a
monolayer of $CH_3(CH_2)_{20}S(CH_2)_{10}CO_2H$. This estimate is based on the
observation that an increase in both chains of $S((CH_2)_xCO_2H)_2$ by 20
carbons increases the thickness of the film by ~10 Å; thus, at the
same packing density, the increase in one chain by this number of
carbons would produce only approximately a 5-Å increase in
thickness. Although an increase in thickness of this magnitude is
not easily detected, given the uncertainty in our measurements,
there is still no evidence of a systematic increase in thickness
with n in Figure 6. Values of thickness for films of unsymmetrical
dialkyl sulfides of the structure $CH_3(CH_2)_{11}S(CH_2)_nCH_3$ responded
similiarly with no obvious increase observed in thickness with
variations of chain length by 6 carbons (n = 11 to n = 17). We
infer either that the data are anomalous in some way (e.g. a
compensation effect due to the adsorption of water on these films
as a function of their hydrophobicity and chain length), or that
the two-dimensional packing density of the unsymmetrical dialkyl
sulfides is even lower than that of the symmetrical dialkyl
sulfides. The latter inference is supported by the relatively good
comparison of values of thickness (unsymmetrical but with chains of
equal length) for films of the sulfide $CH_3(CH_2)_{15}S(CH_2)_{15}CO_2H$
(13.4, 14.7, 13.9 Å for three samples) with the corresponding
values of thickness for films of $S[(CH_2)_{15}CO_2H]_2$ (13 Å) and by

previous reports of the effects of chain length compatibility on the packing of surfactants at the air-water interface.[51]

In general, we use ellipsometric thickness primarily as a measure of reproducibility and as an initial estimate of film quality. For these qualitative uses, it is a valuable technique; internal comparions made using it are (with the possible exception of the unsymmetrical dialkyl sulfides) apparently valid and useful; to derive quantitative information from it will require changes in our experimental procedure and interpretation.

Kinetics of Monolayer Formation. We have not studied the kinetics of formation of monolayers carefully, but have determined conditions in which reproducible, equilibrium properties can be obtained (Figure 7). Both wettability and thickness reach constant values after ~60 min; the major part of the formation seems to be accomplished in the first 30 min. Monolayers used for other studies were prepared by allowing the adsorption to proceed from methanol or ethanol at room temperature for 12-36 h. This time is probably much longer than that required to reach equilibrium; in other experiments, extensive equilibration between preformed monolayers and organosulfur compounds in solution has occurred over this time.[41]

X-Ray Photoelectron Spectroscopy. Obtaining reliable XPS data for the monolayer films proved consistently troublesome, until it became clear that it was necessary to use low X-ray intensities and low temperatures to minimize beam stimulated desorption and damage to the monolayer films. Previous
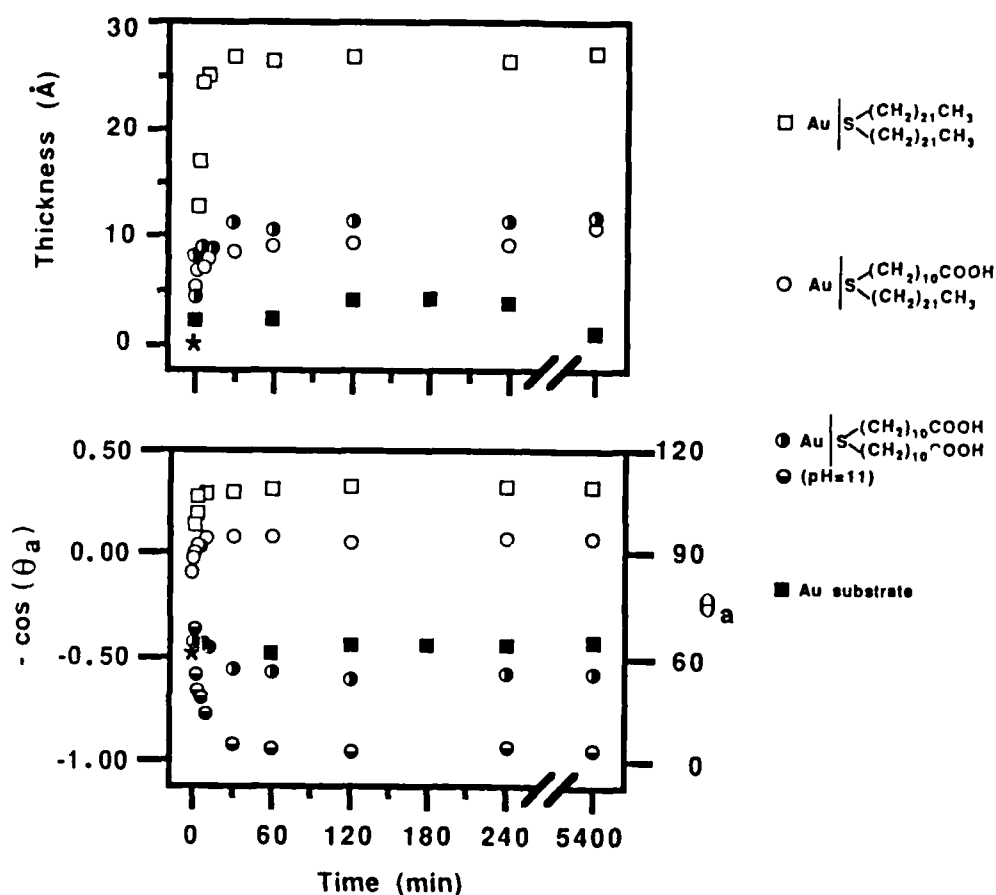
Figure 7. Kinetics of formation of representative films. The upper graph is a plot of thickness (by ellipsometry) as a function of time of adsorption. The lower graph is a plot of contact angle (deionized water, pH = 5.6, unless otherwise specified) as a function of time of adsorption. Values of contact angle at pH 11 were measured with 0.05 M Na_2HPO_4 phosphate buffer. The asterisks represent values for all samples before exposure to the solution containing the organosulfur compound.
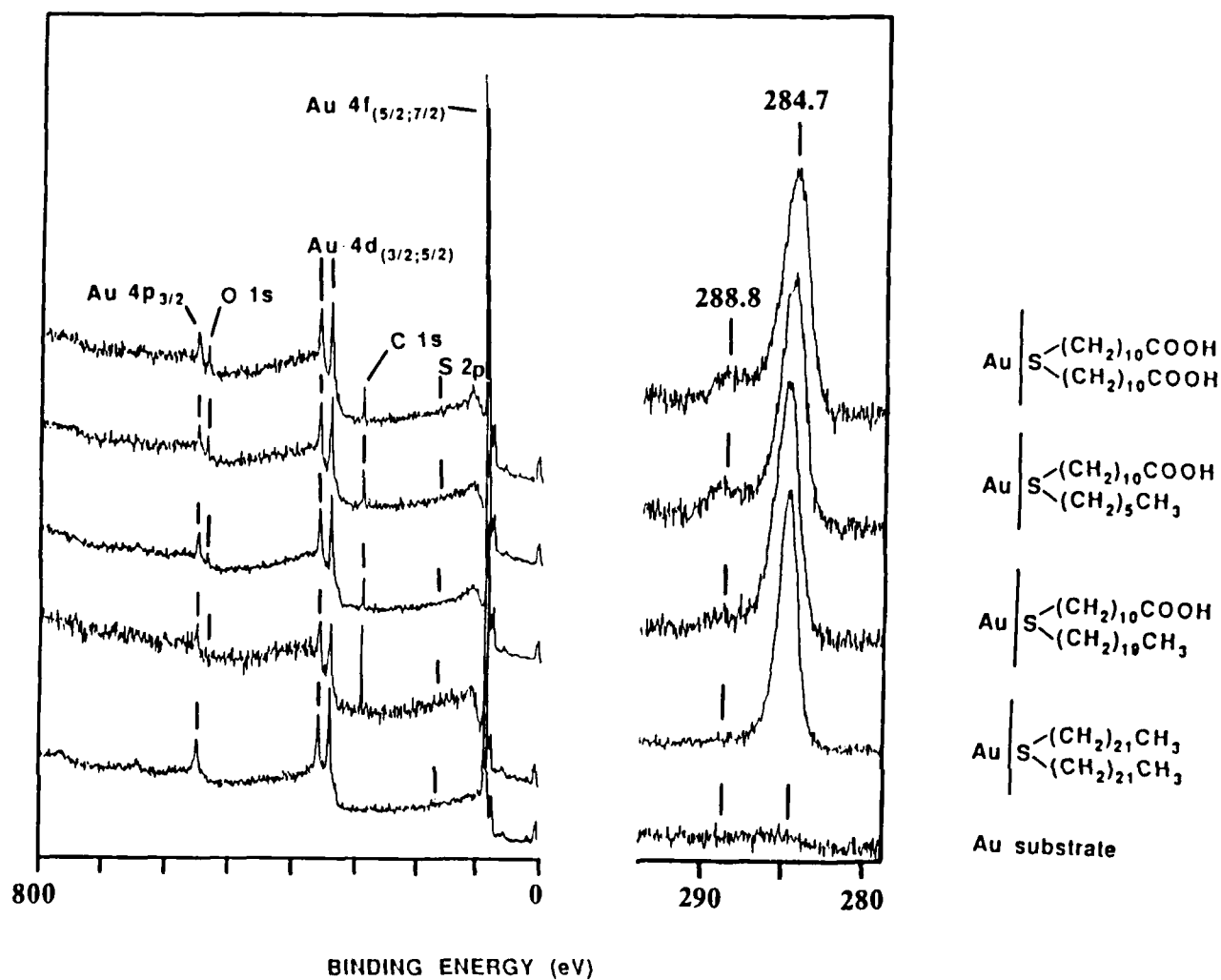
Figure 8. X-ray photoelectron spectra for representative films adsorbed onto gold. Left, Survey XPS spectra. Right, Spectra of the C 1s region. The signals at 288.8 eV are attributed to carboxylic acid groups and at 284.7 eV to the carbon atoms of the alkyl chains.

investigators have also observed serious decomposition of an adsorbed layer of xanthates on copper at high X-ray fluxes.[52] Figure 8 shows spectra for a series of samples: three points are particularly relevant. First, the gold substrate transferred directly from the evaporator to the spectrometer showed little evidence of carbon, oxygen, or sulfur on the surface. This result was not typical, however; most "clean" gold surfaces showed a peak at ~285 eV (referenced to Au 4f 7/2 at 84.0 eV) due to adventitious carbon adsorbed on the surface. Second, the samples of monolayers containing carboxylic acid groups showed clear indications of the CO_2H carbon of the sample in the form of a broad (FWHM ~ 1.6 eV) Gaussian peak at a binding energy of about 289 eV superimposed on a linear background. The identification of this peak is important because certain of these samples showed neither a titratable carboxylic acid nor the presence of a carbonyl stretch in their IR spectra. Independent confirmation is provided by examination of the O_{1s} region: intensity is only seen here in the presence of carboxylic acid groups in the monolayer. Third, the monolayer samples show little intensity attributable to sulfur. The absence of a sulfur peak is due both to its low concentration and cross-section as well as to the low intensity of the X-ray beam and corresponding low signal-to-noise in these spectra. Spectra run on this instrument and on a different instrument at higher X-ray intensity clearly show the expected presence of sulfur. The important conclusion from these studies is only that, so far as XPS can indicate, the monolayers have the composition expected on the

basis of the dialkyl sulfides used in their preparation. This conclusion is important in indicating that the monolayer on the surface is not formed by reaction or decomposition of these dialkyl sulfides, or by formation of a monolayer by selective adsorption of a low-concentration impurity present in the dialkyl sulfides. Preliminary data obtained using the second photoelectron spectrometer are included in the Experimental Section for comparison with the data in Figure 8.

Infrared Reflectance Spectroscopy (IRS). Figure 9 shows IRS data for four dialkyl sulfides adsorbed on gold. There are two important points to be made about the spectra. First, the major absorption peaks roughly match ones observed for the pure sulfides. We interpret this observation to mean that the adsorption process negligibly perturbs the chemical bonds of the sulfide molecules, in agreement with the XPS data above. Second, replicate samples showed spectra with small variations in peak intensities, shapes, and positions, particularly for the modes associated with the carboxyl group. This result supports our contention that exposed polar surface groups are susceptible to adsorption of contaminant species from the ambient environment (e.g., water and volatile organics). Interpretations necessary to establish relevant structural features follow below. More detailed interpretations and discussions will be presented elsewhere.

The CH_2 groups of all the sulfides studied exhibited C-H stretching frequencies with values that were several cm-1 higher than those of the pure crystalline compounds. This shift in

Figure 9.   Polarized infrared external reflection spectra of
representative films prepared by spontaneous assembly
of diundecylsulfide bis-(11-carboxyundecyl)sulfide,
11-methylthioundecanoic acid, and 11-hexadecyl-$\underline{d}_{33}$-
thioundecanoic acid adsorbates from dilute ethanol
solutions onto gold. Signals at 2925 cm^{-1} and 2923 cm^{-1}
are attributed to the CH_2 asymmetric stretch, those at
2853 cm^{-1} and 2860 cm^{-1} to the CH_2 symmetric stretch
those at 1736 cm^{-1} and 1718 cm^{-1} to the C=O stretch,
and those at 2200 cm^{-1} and 2100 cm^{-1} to the CD_2
asymmetric stretch and CD_2 symmetric stretch
respectively.   Note the absence of an observable C=O
stretch in the spectrum of the film prepared from
11-hexadecyl-$\underline{d}_{33}$-thioundecanoic acid, even though
signals attributable to the methylene and
deuterium-labeled methylene chains are observed.
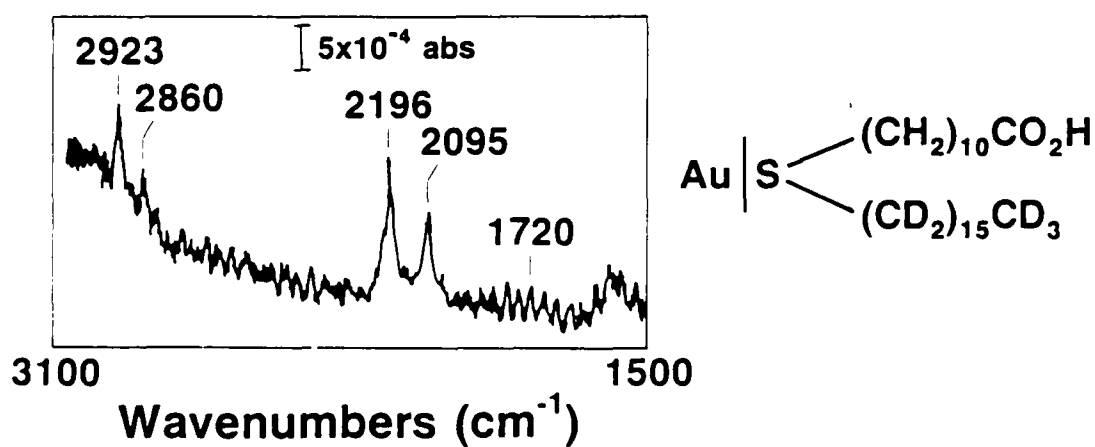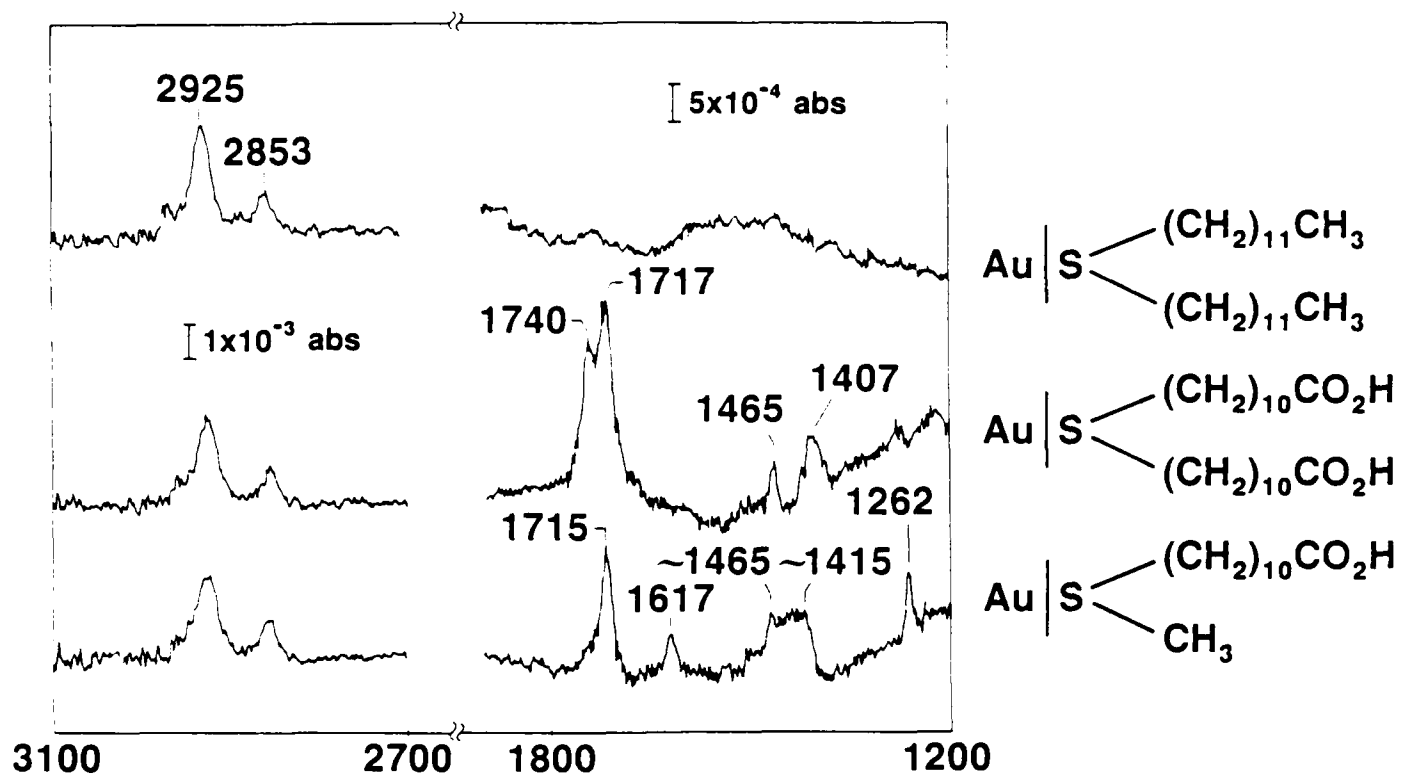
frequency suggests that the chains are more loosely packed and liquid-like in the monolayers than in the pure solid phase[10]. This conclusion is in godd agreement with the wetting and ellipsometry results.

It is interesting that the symmetrical carboxylic acid-terminated disulfide showed two distinct carbonyl peaks at 1718 and 1736 cm^{-1}. The probable origin of the splitting in the symmetrical structure is hydrogen-bonding between the carboxylic acid groups.

Initial efforts to obtain a spectrum for $CH_3(CH_2)_{15}S(CH_2)_{10}CO_2H$ showed no carbonyl stretch. We synthesized the deuterated compound shown in Figure 9 and prepared a monolayer from it, in order to establish that a monolayer of the expected material was being produced. Method A (eq 1) was used to prepare this unsymmetrical dialkyl sulfide: that is, it was prepared by reaction of $CD_3(CD_2)_{15}Br$ with the corresponding protonated thiol. This method was used to ensure that the deuterium label would not be associated with sulfur unless the displacement reaction had occurred. The infrared spectrum (Figure 9) clearly shows peaks at 2095 and 2196 cm^{-1}, as expected for C-D vibrations (the CD_3 stretches are too weak to be resolved). No peak in the 1720 cm^{-1} region was visible. We infer that the expected monolayer was present on the gold surface, but that the broad carbonyl stretch was weak or absent in this adsorbed layer.

The considerable effort to prove the presence of this monolayer on gold was stimulated by the observation that its

carboxylic acid group showed virtually no influence on the wettability of the monolayer. This result was crucial to our effort to make monolayers in which the carboxylic acid group was hidden by longer, methyl-terminated, alkyl chains in unsymmetrical sulfides, and we wished to establish unequivocally that the monolayer comprised the unsymmetrical dialkyl sulfide we desired, rather than an adventitious, strongly adsorbing impurity present in the system. Having established that the intended component did make up the monolayer, the question was then: Why is a carbonyl stretch not observed? The concentration of carboxylic acid groups in this system is half that in the diacid system (with the assumption that the unsymmetrical and diacid systems have similiar packing densities) and the signal-to-noise in the spectra (Figure 9) is such that this concentration should be observable. There then seem to be two plausible answers. First, the adsorption band may be quite broad for some reason (strong hydrogen bonding or the existence of several different environments for the carboxylic acid groups), and the band is simply not detectable at the signal-to-noise levels achieved in these samples. Alternatively, these results might be rationalized on the basis of a parallel orientation of the carboxylic acid carbonyl group with respect to the plane of the gold substrate. For reflection IR spectroscopy, the strongest adsorption occurs for vibrational modes with transition dipoles oriented perpendicular to the gold surface and virtually no absorption occurs for dipoles parallel to the surface. It is conceivable in some of these samples that, for some reason,

the carboxylic acid groups tend to orient parallel to the substrate. If for example, this orientation maximized hydrogen bonding, then the bands would be diminished in amplitude, due to both broadening and orientation, and might thus be lost in the noise. There appears to be no a priori reason to expect this particular orientation and independent evidence is needed for confirmation. Whatever the origin of the low intensity of this absorption, there must be some significant difference between the structures of the unsymmetrical dialkyl sulfides having one carboxylic acid-terminated chain and the symmetrical bis(carboxylic acid-terminated) sulfides, since the latter do show distinct IR absorbance in the carbonyl region.

The Contact Angle of Water on Dialkyl Sulfide Monolayers. Figure 10 summarizes the measured wetting properties of a number of unsymmetrical monolayers having the structure $CH_3(CH_2)_{10+m}S(CH_2)_{10}CO_2H$ prepared by adsorption from ethanol. Similiar data were observed for films prepared by adsorption from THF. The index "m" indicates the difference in the number of methylene groups between the methyl-terminated and the carboxylic acid-terminated chains; m is positive if the methyl-terminated chain is longer. For comparison, this figure also includes data for two homologous series of reference compounds (Figure 4): metnyl-terminated and carboxylic acid-terminated symmetrical dialkyl sulfides. Retreating contact angles, θ_r, showed the same trends as advancing contact angles, θ_a, but are uniformly smaller (see the Experimental Section).

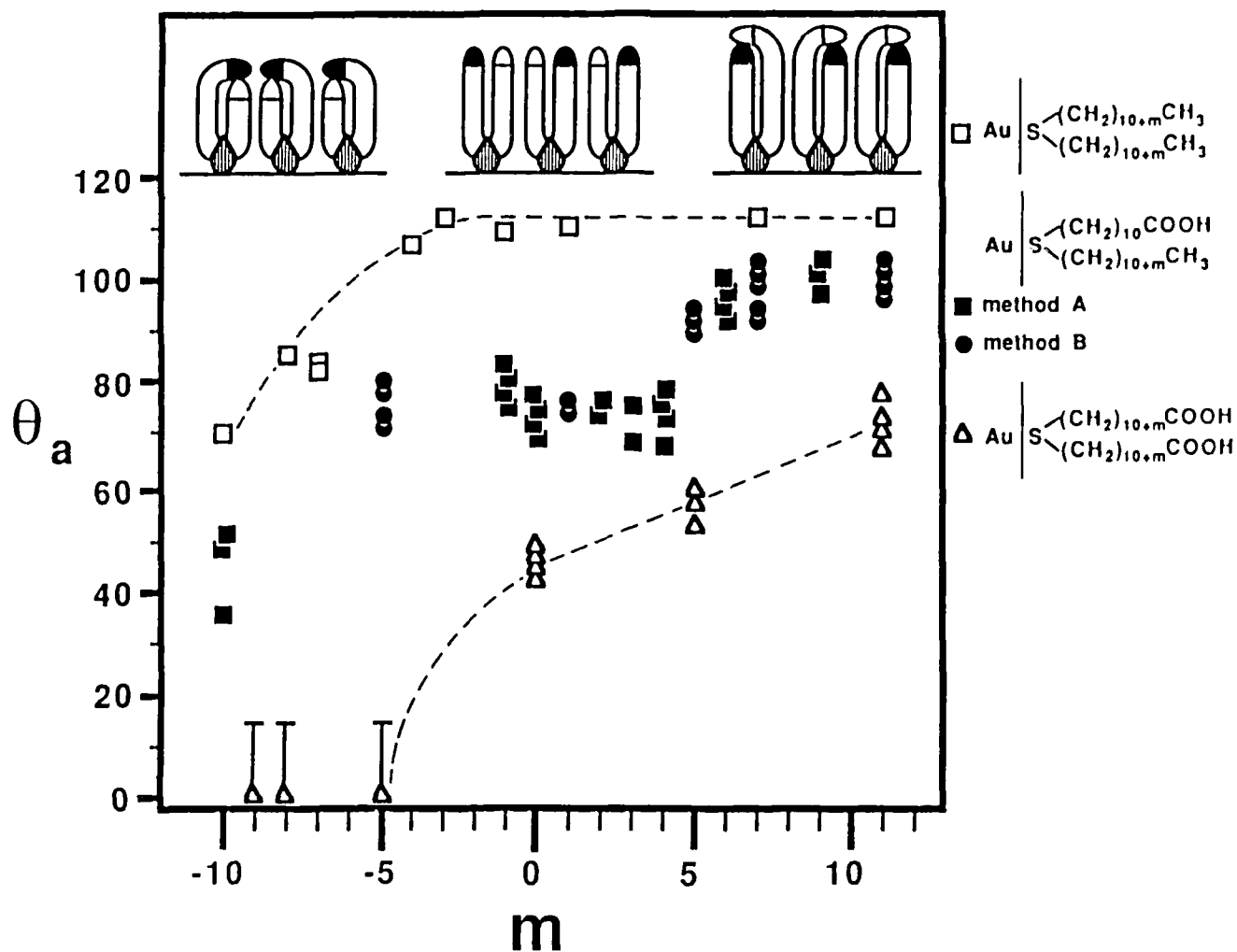Figure 10. Advancing contact angles (deionized water, pH = 5.6)

for monolayer surfaces prepared from

11-n-alkylthioundecanoic acids, adsorbed onto gold.

Solid squares represent adsorbates prepared by method A

and solid circles those prepared by method B (eq 1).

Open symbols represent values for the interfaces

presented by symmetrical dialkylsulfides adsorbed onto

gold, and are included for reference.

Methyl-terminated systems (both symmetrical sulfides and methyl-terminated thiols; Figure 4) maintain a high hydrophobicity until the number of methylene groups between the sulfur atom and the methyl groups falls below approximately 5. The shorter films become progressively more hydrophilic, reaching a value of θ_a ~70° for $(CH_3)_2S$. We have not established the origin of this decrease in hydrophobicity with decreasing chain length in any detail. It is plausible to ascribe it to the influence of local gold-sulfur or sulfur-carbon bond dipoles on contacting water, to the interaction of the highly polarized metal with the water, or, perhaps, to direct contact of the water with sulfur and gold atoms by penetration between adsorbed organosulfur molecules. Independent electrochemical studies of thiols on gold electrodes indicate that the density of pinhole defects increases as the chain length of alkyl thiols decreases.[10]

The carboxylic acid-terminated systems are more polar than the methyl-terminated systems over the full range of chain lengths examined. The carboxylic acid-terminated thiols are uniformly wettable: $\theta_a \simeq 0°$ for all systems (Figure 4). Carboxylic acid-terminated symmetrical dialkyl sulfides show large variation in their wettability with chain length. For short chain lengths (four and fewer methylene groups) θ_a is also $\simeq 0°$. For chains having 10 or more methylene units between the sulfur and the carboxylic acid group, the values of contact angle increase from ~40° $((CH_2)_{10})$ to ~80° $((CH_2)_{21})$. For comparison, the contact angle of water on polyethylene, $(CH_2)_n$, is $\theta_a \simeq 103°$. The simplest

interpretation of the data for the carboxylic acid-terminated symmetrical dialkyl sulfides, and one consistent with other data, is that these systems should be considered as viscous liquid or liquid crystalline films, and that the increasing hydrophobicity correlates with the increasing dilution of the polar carboxylic acid moieties with non-polar methylene groups.

The data for unsymmetrical dialkyl sulfides containing both methyl- and carboxylic acid-terminated chains are, as expected, qualitatively intermediate between those of the corresponding symmetrical methyl-terminated and carboxylic acid-terminated dialkyl sulfides. The question of central concern is whether there is any evidence in the data for the unsymmetrical dialkyl sulfides that suggest structure in the dimension perpendicular to the mean plane of the gold substrate, and implying systematic covering and revealing of the polar carboxylic acid group with changes in the length of the methyl-terminated chain. The most interesting feature of the data from the vantage of this question is the sharp drop in θ_a observed between m = 6 and m = 4. This sharp increase in hydrophilicity with decreasing length in the methyl-terminated chain is very unlike the smooth curves observed for the symmetrical dialkyl sulfides. The scatter in the data is appreciable, and not all compounds were examined for possible artifacts due to contaminating thiols. Nonetheless, data obtained using dialkyl sulfides prepared by both methods A and B are compatible. We conclude that the trends in these data are real, and establish a significant change in hydrophobicity with a small change in the

structure of the adsorbed unsymmetrical dialkyl sulfide. They are compatible with (but do not demand) the unveiling of the polar carboxylic acid group as the methyl-terminated chain becomes comparable to the carboxylic acid-terminated chain in length.

A second feature of the data for the unsymmetrical dialkyl sulfides suggesting structure is the value of θ_a for long methyl-terminated species. These values ($\theta_a \simeq 100^O$) are comparable to those for polyethylene, and establish that the carboxylic acid groups in these systems are completely hidden from water. Thus, a $CH_3(CH_2)_{10}$ group is apparently sufficiently large to mask completely an underlying carboxylic acid moiety. A similiar effect has been observed for long-chain esters of the alcohol derived by reduction of polyethylene-carboxylic acid $(PE-CO_2H)$[15] and for adsorbed monolayers having the structure $CF_3(CF_2)_n(CH_2)_{16}CO_2H$.[27] The limiting value of θ_a observed for the unsymmetrical sulfides having long methyl-terminated chains ($\theta_a \sim 100^O$) is less than that observed for an interface presentinj almost exclusively methyl groups ($HS(CH_2)_{16}CH_3$, $\theta_a = 115^O$) and comparable to one comprising predominantly CH_2 groups (polyethylene, $\theta_a \sim 103^O$). This difference between the contact angle of water on methyl and methylene-containing interfaces may arise from the greater disorder in the latter case, reducing the lateral interactions, and increasing the exposed surface area.

Interpretation of the data for unsymmetrical dialkyl sulfides having "short" methyl-terminated chains is less straightforward. Experimentally, the scatter in these data was greater than that for

other systems examined. We note here some of the features that might contribute to the interfacial free energy in these monolayer films. First, the adsorbed films in these systems are sufficiently thin that they are more hydrophilic than thicker systems, independent of any structure in the organic layer (presumably due to interactions between water and the gold and/or gold-sulfur interphase). Second, the stability of the hydrocarbon-air interface is greater than that of a carboxylic acid-air interface; this order of relative stabilities is probably reversed for interfaces with water. There is thus a thermodynamic driving force tending to reorganize a mobile interface in these unsymmetrical sulfides to one in which the interfacial free energy has been minimized by changing the composition of the interface to maximize the number of CH_2/CH_3 groups (for a non-polar interface) or CO_2H groups (for a polar interface).

Contact Angle Titration. Previous, extensive studies of interface-functionalized polyethylene have established the utility of measurements of θ_a as a function of pH as a method of examining the characteristics of interfacial acids and bases.[13-15] Figure 11 shows relevant data for the dialkyl sulfide-based monolayers studied here.

The long-chain, symmetrical methyl-terminated dialkyl sulfide $(CH_3(CH_2)_{21})_2S$ shows no change in contact angle with pH, as expected for an interface having no ionizable groups. The contact angle with water of the symmetrical, carboxylic acid-terminated dialkyl sulfide $(HO_2C(CH_2)_{10})_2S$ at high values of pH is $\theta_a \simeq 20°$,

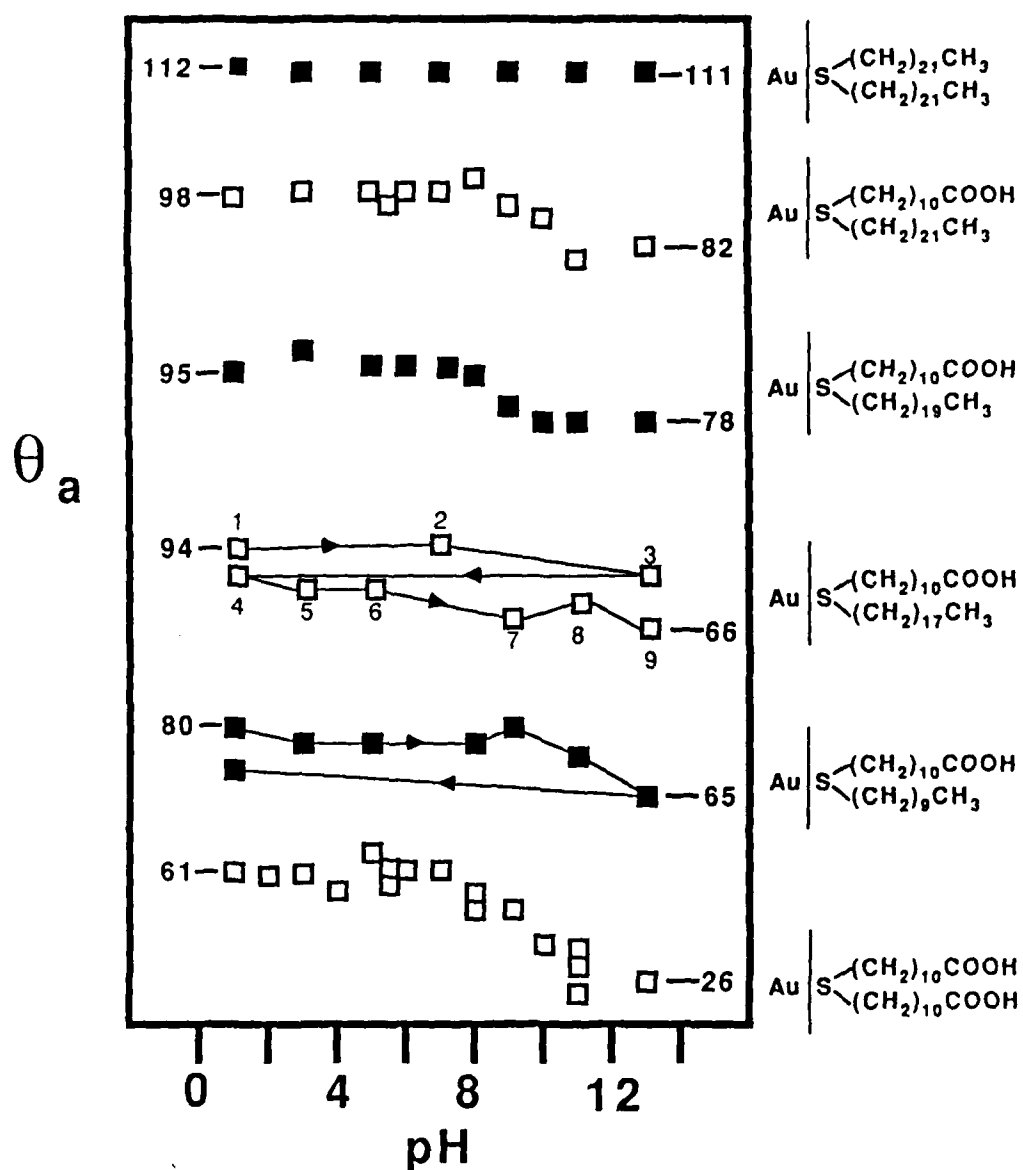Figure 11. Advancing contact angles of selected aqueous buffers for monolayer surfaces prepared from didocosyl sulfide, 11-n-docosylthioundecanoic acid. 11-n-eicosylthio-undecanoic acid, 11-n-octadecylthioundecanoic acid, 11-n-decylthioundecanoic acid, and bis-(11-carboxy-undecyl) sulfide adsorbed onto gold. Contact angles were measured within 1 minute and are not necessarily equilibrium values.

and is significantly larger than the value of $\theta_a = 0^\circ$ observed for carboxylic acid-terminated thiols. This difference indicates that the interface of the dialkyl sulfide-based system is less ordered than that for the thiols. The dialkyl sulfide monolayer apparently presents carboxylic acid groups to water in a matrix of methyl and methylene groups. Data that are numerically very similiar are observed for polyethylene carboxylic acid[13] and for certain carboxylic acid-terminated silanes on glass.[49]

The data for the unsymmetrical dialkyl sulfides are interesting primarily because the carboxylic acid groups in these systems do not seem to titrate:[13] the values of θ_a do not seem to demonstrate a reversible change in the wettability of the film surface with changes in the pH of the contacting water. In these monolayers incorporating long methyl-terminated chains ($CH_3(CH_2)_{21}$, $CH_3(CH_2)_{19}$, and $CH_3(CH_2)_{17}$) the values of θ_a at low values of pH are comparable to those for polyethylene, and suggest no influence of the carboxylic acid group on the monolayer-water interfacial free energy. We believe that the small but significant decrease in θ_a with pH in these systems reflects instability of the films at high values of pH, rather than any effect of ionization of the carboxylic acid group. For example, the data for $CH_3(CH_2)_{17}S(CH_2)_{10}CO_2H$ represent two sets of titrations carried out at the same location on the film. The points represented by numbers 1 through 3 were carried out, the film was washed, and then points 4 through 9 were obtained in the same location. The drop in contact angle with increasing pH in this system is thus partially

irreversible.

The data for the unsymmetrical dialkyl sulfide containing methyl-terminated and carboxylic acid-terminated chains of equal length--$(CH_3(CH_2)_9S(CH_2)_{10}CO_2H$--shows an interesting combination of effects. The value of θ_a at pH 1 (80°) is significantly lower than that for polyethylene and indicates a significant influence of the polar carboxylic acid group on the wettability of the surface. Nonetheless, the contact angle of water on this film shows only a weak or nonexistent dependence on pH: the drop in θ_a is of the same magnitude as that observed for films having completely buried carboxylic acid groups, and probably reflects primarily etching of the organic monolayer at high values of pH rather than significant ionization of the carboxylic acid group. We believe that the absence of a significant change in θ_a with pH is due to the low dielectric constant of the environment in which the carboxylic acid groups are located, and perhaps to steric hindrance to solvation of carboxylate anions at this interface, with a resulting increase in effective $p\underline{K}_a$ of the carboxylic acid group to a magnitude that is unreachable using aqueous solutions in the usual range of values of pH. The acidity of carboxylic acid groups buried a few ångstroms within a low-dielectric constant medium is expected to decrease strongly due to the much lower dielectric constant relative to water. For example,[53] the value for the $p\underline{K}_a$ of acetic acid is 247 in the gas phase, 11.9 in dimethyl sulfoxide ($\varepsilon = 46.7$), and 4.8 in water ($\varepsilon = 78.3$). The effect of the local environment on the acidity of carboxylic acid groups is also well-documented.[53-59]

The environment of a carboxylic acid group buried 5-10 Å beneath the surface of a monolayer might plausibly resemble that of 2,4,6-tri-_tert_-butylbenzoic acid[55] or 2,4,6-tri-_tert_-butylphenol;[60] these compounds are difficult to ionize in aqueous solution.

The absence of a significant contact angle titration in this monolayer might also reflect reconstruction of the film surface, or electrostatic repulsion of carboxylate ions through a low dielectric constant medium.

Interfacial Reconstruction. We infer from the data in this paper that monolayer films based on dialkyl sulfides are relatively disordered. If the organic components of these films are considered as fluids they could, in principle, rearrange to minimize the interfacial free energy when placed in contact with different environments.[61] One might then be faced with different structures, depending on the environment. This phenomenon of surface reconstruction is well established for polyethylene carboxylic acid and its derivatives, although the reconstruction is kinetically slow at room temperature.[16]

We have tried to establish the importance of surface reconstruction in determining the characteristics of the interface between monolayers of dialkyl sulfides on gold and low or high dielectric constant media. The results of these efforts do not indicate any large influences of reconstruction, but are open to at least two interpretations: first, that there is _no_ reconstruction, that is, the characteristics of the interface are essentially independent of the environment; second, that reconstruction occurs

too rapidly to be detected.

With the exception of $CH_3S(CH_2)_{10}CO_2H$ and $S((CH_2)_{10}CO_2H)_2$, exposure of monolayer films to argon or air (low dielectric constant media) or water (a high dielectric constant medium) for prolonged periods at room temperature resulted in no change in the interfacial characteristics of the monolayers (as measured by their contact angle with water). These two carboxylic acid-terminated dialkyl sulfides show small changes in interfacial characteristics reflecting the previous history of the sample. Figure 12 shows the data. In brief, samples conditioned by exposure to argon for periods of 2-24 h at room temperature are consistently slightly more hydrophobic than those conditioned by exposure to water for similiar periods of time. These data are consistent with a small degree of interfacial reconstruction reflecting preferential segregation of the polar carboxylic acid groups at the polar organic-water interface and expulsion of these groups from the non-polar organic-argon interface. These effects, however, are relatively small ($\Delta\theta_a \sim 5$-10°). Moreover, it is difficult to exclude some influence from a small amount of adsorption of a volatile, non-polar contaminant in the experiments involving conditioning in argon. Experimental attempts to facilitate reconstruction of these monolayer films by heating them in argon for 1 h at 80 $^{\mathrm{O}}$C (the melting point of the partial dialkyl sulfide is 110.0 -111.5 $^{\mathrm{O}}$C) resulted in desorption of the film from the surface (as reflected in the ellipsometric thickness).
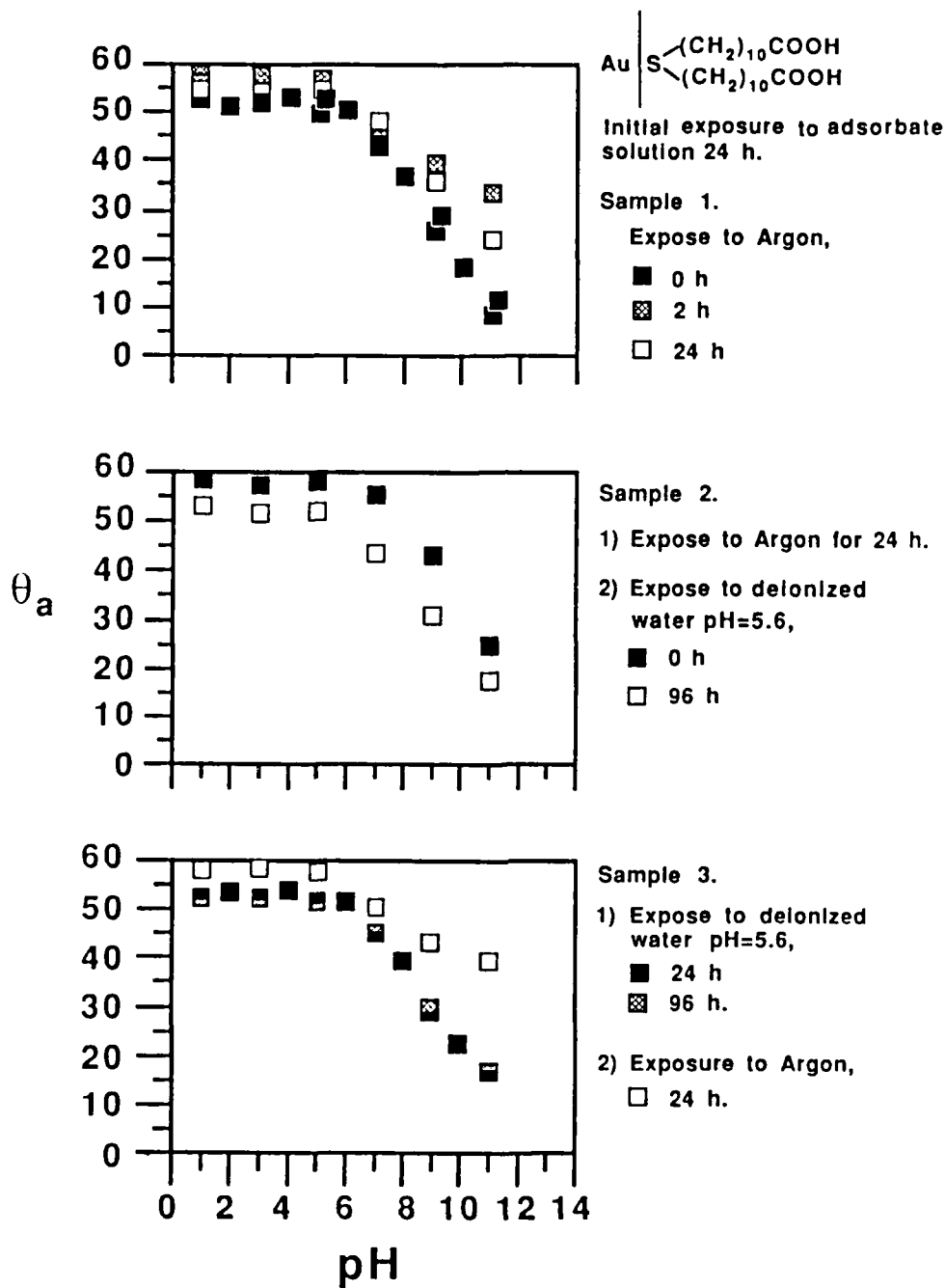
Figure 12. Effect of exposure to air on the advancing contact angles of selected aqueous buffers for monolayer surfaces prepared from di(11-carboxyundecyl) sulfide adsorbed onto gold.

Discussion

The data summarized in this paper lead to two broad conclusions concerning monolayers formed by adsorption of dialkyl sulfides on gold.

First, exposure of clean gold under normal laboratory conditions to solutions of a number of dialkyl sulfides results in rapid formation of equilibrium monolayers. This organic monolayer is reasonably stable to exposure to aqueous solutions, except at high values of pH. The system is amenable to wide manipulation by means of changes in the composition of the dialkyl sulfide: the major experimental point in the reproducible formation of these monolayers is to purify the dialkyl sulfide in such a way as to avoid contamination by the more strongly (and perhaps rapidly) adsorbed thiols.

Second, self-assembled monolayer films formed from dialkyl sulfides are significantly less densely packed and less ordered than those prepared by adsorption of alkyl thiols. Although the evidence for structural order in monolayers formed from alkyl thiols is only sketched in this paper, this conclusion is based on two types of observations: First, the thicknesses of the films formed from dialkyl sulfides are generally lower than those formed from analogous alkyl thiols as measured by ellipsometry, and smaller incremental increases in thickness are observed on increasing the length of the polymethylene chains. Second, the carboxylic acid-terminated dialkyl sulfides show much higher contact angles with water than do carboxylic acid-terminated

thiols; the methyl-terminated dialkyl sulfides exhibit slightly lower contact angles with water than do methyl-terminated thiols.

We conclude that the most useful physical model for the dialkyl sulfide films is that of a thin liquid, liquid crystal, or glass anchored to the gold support via the gold-sulfur coordinate bond (Figure 13). Even if liquid or glassy, these systems cannot be fully isotropic: order imposed by the geometry of attachment of the dialkyl sulfide moiety to the gold surface must extend to some extent throughout these very thin films.

We have no direct measure of properties such as microscopic viscosity in these monolayers. Direct measure of viscosity using the usual techniques based on spin labels and fluorescent depolarization are impractical, due to the close proximity of the monolayer to the conducting metal. Indirect efforts to detect slow processes reflected in environmentally dependent reconstruction produced ambiguous results. The organic dialkyl sulfides from which the monolayers are formed are solids with melting points of 50-130 $^{\circ}$C, and we anticipate that the films have high internal viscosity and should be considered as thick liquids or glassy solids based on previous studies of related systems.[62,63,64]

Even given the significant disorder that apparently characterizes dialkyl sulfides adsorbed on gold, it is possible to demonstrate a significant degree of control over the average structure of the film at the scale of Ångstroms. Thus, unsymmetrical disulfides having a shorter carboxylic acid-terminated arm and a longer methyl-terminated arm adsorb in
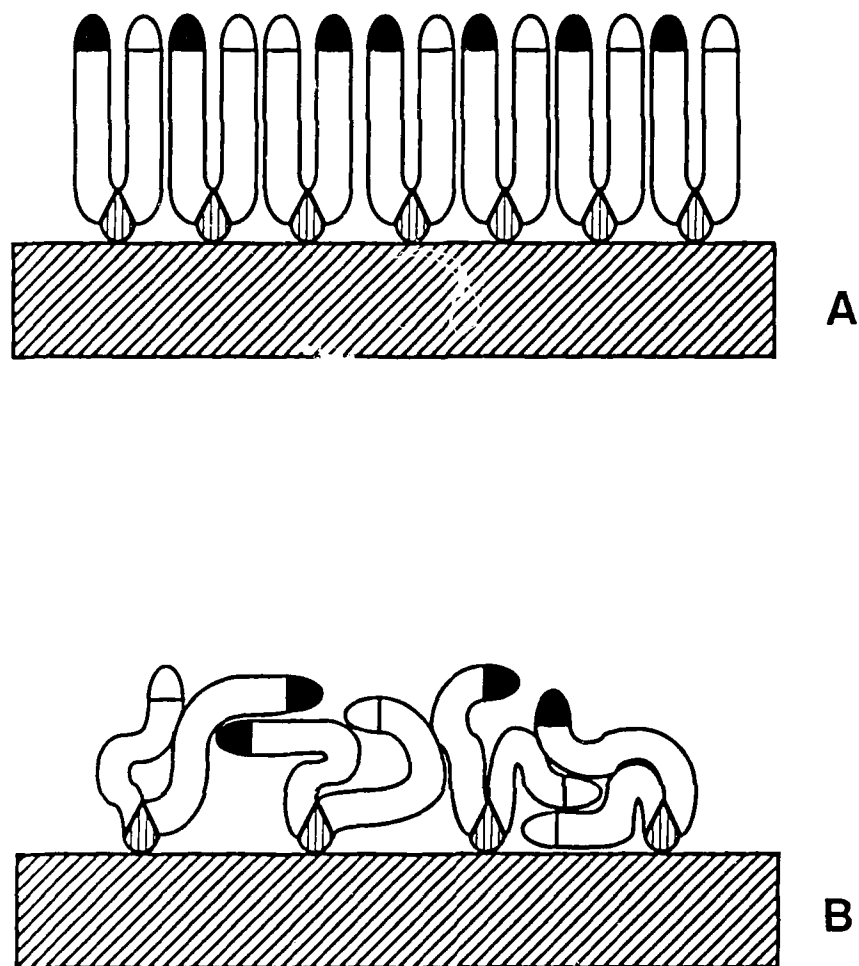
Figure 13. Schematic illustration of the influence of the ordering of films on the interfaces presented by perfectly ordered films (A) and the loosely ordered sulfide films in this study (B).

such a way that the polar carboxylic acid group is effectively
completely screened from contact with an aqueous liquid phase (to
the extent that the acid group does not influence the contact
angle) when the two chains differ by only approximately five
methylene units in length. The carboxylic acid groups are
effectively fully exposed when the two chains have the same length.
These monolayers thus represent a successful example of designed
modification of a macroscopic physical property (wettability by
water) by molecular-scale variation of the structure of molecular
constituents. Although this particular type of monolayer does not
show the degree of structural control afforded by a rigid organic
monolayer or a single crystal, the degree of control of composition
over the monolayer in the direction perpendicular to the mean plane
of the supporting metal is highly encouraging for efforts to
prepare organic surfaces/interfaces having structures sufficiently
well-defined to form the basis for physical-organic studies of
interfacial structure-property relations.

A valuable consequence of these studies is further
verification of the short-range character of the forces involved in
determining wetting. This work yields several independent examples
of thin films shielding an underlying solid from interaction with a
contacting liquid. Thus, it appears to take an alkyl chain of
about five methylene units in these films to shield water from the
influence of the gold-sulfur interphase. Approximately five
methylene units are also required to shield the carboxylic acid
moiety in an unsymmetrical dialkyl sulfide. Previous studies of

polymer interfacial esters[15] and terminally-fluorinated fatty acids[27] suggest similiar numbers. Thus, in no case does the influence of the underlying substrate seem to penetrate more than approximately 10 Å of intervening condensed phase in influencing the contact angle of a wetting liquid phase.

This conclusion is important in confirming the short-range character of wetting, and in emphasizing the value of studies of wettability in investigations requiring high surface selectivity/specificity. The relatively large quantity of hydrocarbon apparently required to cover the gold-sulfur interphase in these systems may reflect either the large head-group area that must be covered, or significant permanent electric dipole effects having a longer range than the short-range van der Waals interactions that appear to dominate most wetting.[65]

The conclusion that the interactions dominating wetting are short-range (≤ 5 Å) in these systems are compatible with results using direct measurements based on surface force balance techniques.[29] This latter technique yields more quantitative data than wetting, but is presently interpretable in detail only with relatively simple systems. Further, it is experimentally difficult. Wetting has the advantage of experimental simplicity, applicability to complex systems, and indirect interpretability in terms of local chemical phenomena in the interphase (for example, ionization of carboxylic acid groups).

Experimental Section

General. Chemicals purity; source (A = Aldrich; solvent of recrystallization, or Used As Received) were: 11-bromoundecanoic acid (99%, A, hexanes); thiolacetic acid (99%, A, UAR); 1-hexanethiol (96%, A, UAR); 1-dodecanethiol (98%, A, UAR); 1-hexadecanethiol (technical grade 92%+, A, ethanol); 1-Octadecanethiol (98%, A, ethanol); 1-bromodecane (A, UAR); 1-bromoundecane (A, UAR); 1-bromotridecane (A, UAR); 1-bromotetradecane (A, UAR); 1-bromopentadecane (A, UAR); 1-bromooctadecane (98%, A, ethanol); 1-bromoeicosane (Alfa, hexanes) and 1-bromodocosane (97%, Alfa, hexanes); 1-heptadecanol (98%, A, UAR); 16-hydroxyhexadecanoic acid (A, UAR); 1-bromohexadecane-d_{33} (D33, 98%, Cambridge Isotope Laboratories, UAR); di-n-butyl sulfide (Baker, UAR); di-n-octadecyl sulfide (Pfaltz and Bauer, hexanes); bis-(1-carboxymethyl)sulfide (98%, A, water); bis-(2-carboxyethyl)sulfide (99%, A, water); 11-bromo-1-undecanol (98%, A, hexanes); lithium sulfide (Alfa, UAR). Sources of materials used to prepare gold substrates were gold (99.9%, Englehard; 99.99% Aesar; 99.999% Materials Research Corporation), chromium (99.999% obtained from either Materials Research Corporation or R.D. Mathis); silicon wafers (Monsanto). Argon, absolute ethanol (U.S. Industrial Chemicals Co.), absolute methanol (analytical grade, Mallinckrodt), Methylene chloride (Fisher) and tetrahydrofuran (Fisher, reagent grade) were used as received. Cyclohexane (Aldrich, Gold Label), hexanes (Aldrich, Gold Label) and hexadecane (99%, Aldrich) were purified by

percolation twice through neutral, grade 1, activated alumina and degassed with argon. Solvents purified in this manner passed the Bigelow test.[66]

Water was passed through an ion exchanger (Cole Parmer) and distilled in a Corning Model AG-1b glass distillation apparatus. The buffers used (0.05 M except where stated) were as follow: pH 1, 0.1 N HCl; pH 2, sodium phosphate; pH 3, malonic acid; pH 4, sodium phosphate; pH 5, acetic acid; pH 6, sodium phosphate; pH 7, sodium phosphate; pH 8, sodium phosphate; pH 9, boric acid; pH 10, boric acid; pH 11 sodium phosphate; pH 12, sodium phosphate; pH 13, 0.1 N NaOH.

Silica gel (70-230 mesh ASTM) for Chromatographic adsorption/purification and TLC plates (silica gel 60 F254 pre-coated, layer thickness 0.25 mm) were obtained from E.M. Reagents. The purity of reagents and adsorbates was checked by gas chromatography (Perkin-Elmer 3920B), melting point (uncorrected, Thomas Hoover melting point apparatus), and ^{1}H NMR spectroscopy (using a 250 MHz Bruker or 300 MHz Bruker spectrometer). Elemental analysis was performed by Galbraith Laboratories.

Wafer trays were obtained from Fluoroware, and were used as received as containers in which to store gold substrates.

Preparation of gold substrates. During the course of these studies, gold substrates were prepared in a number of different evaporators using both thermal and electron-beam sources. The thermal evaporators all employed resistively heated tungsten baskets and comprised a home-made diffusion-pumped evaporator

(Harvard University MRL) equipped with a liquid-nitrogen trap operating with a base pressure of 1 X 10^{-6} torr; an NRC Model 3116 diffusion-pumped evaporator (Professors Lobb and Tinkam) equipped with a liquid nitrogen trap and operating with a base pressure of 1 X 10^{-7} torr; a home-built evaporator (Prof. Klemperer) equipped with a liquid nitrogen trap and operating with a base pressure of 1 X 10^{-7} torr, and a modified Varian evaporator (AT&T Bell Laboratories) equipped with a cyro-pump and operating with a base pressure of 10^{-8} torr. The electron-beam evaporator (MIT Microelectronics Laboratory) was a home-built vacuum system utilizing a Sloan Technology electron-beam gun; the evaporator was equipped with a liquid nitrogen trap and operated with a base pressure of 10^{-7} torr. With the exception of the home-made evaporator (Harvard University MRL), all gave similar results. The unsatisfactory results obtained using gold substrates prepared in this evaporator may have been caused by co-evaporation of copper from the electrodes and consequent contamination of the gold substrates. At Harvard and Bell Laboratories, electronic grade, single crystal, (111) silicon wafers (2- or 3-in diameter) were cleaned in hot 1:4 H_2O_2 (30%)/H_2SO_4 and rinsed with distilled, deionized water and absolute ethanol; at M.I.T., the standard RCA cleaning procedure[67] was used. The wafers were coated with 50-150 Å of Cr to promote adhesion and ~2000 Å of Au, as measured by a quartz crystal thickness monitor.

Gold-coated wafers were removed from the evaporator with Teflon-coated tweezers and were stored in wafer trays wrapped in

Parafilm. Gold-coated wafers should be used within one week since they contaminate irreversibly upon prolonged storage. Before use, gold-coated wafers were cut into appropriate sizes (usually 1-1.5 cm in width and 3-4 cm in length) by scoring the wafer on the gold-coated side using a diamond-tip cutter (Brookstone) and breaking the wafer using Teflon-coated tweezers. Silicon dust was blown from the substrates by a stream of argon gas. The gold substrates were then washed three times with ethanol using a 1-mL disposable glass pipette equipped with a rubber bulb and dried in a stream of argon for 5 to 15 seconds. They were used immediately. Gold substrates were examined visually, and by ellipsometry and contact angle in order to determine their suitability for use in the preparation of monolayer films. Suitable substrates for the preparation of monolayer films had the following characteristics: 1) They were visually free of defects. 2) After washing with ethanol they had reproducible ellipsometric properties independent of the location of the spot examined on the substrate. In practice, ellipsometric measurements were taken at 3 locations on the gold substrate that were separated by at least 1 cm. If the polarizer readings fell within a range of $\pm 0.15^{\circ}$ (this range corresponds to about ± 3 Å of a film with an index of refraction of 1.45), the gold was judged to be satisfactory for ellipsometry experiments. 3) Gold substrates that had been washed with ethanol showed θ_a = 55-70° (deionized water, pH = 5.6). The contact angle on freshly evaporated gold-coated wafers after removal from the evaporator was typically θ_a = 60° and increased on storage to about

90°. Gold substrates prepared, treated, and characterized in this manner gave reproducible results.

There are several issues concerning the preparation of suitable gold substrates for these studies. First, precleaning of silicon wafers before the evaporation was critical for preparing gold substrates that were free of visible defects; silicon substrates that were improperly cleaned resulted in gold substrates with visible defects and cloudy regions. Such defects were also observed for films evaporated on glass, so silicon is a preferred substrate.

Second, evaporations of gold onto silicon wafers were carried out in such a fashion as to minimize heating of the wafers during the evaporation process: heating of the wafers could result in diffusion of silicon or chromium through the gold layer. It was not necessary, however, to cool the silicon wafers during the evaporation process in order to prepare suitable gold substrate. In practice evaporations were performed with the silicon wafers located at least 12 in from the evaporation source, at low pressures ($<10^{-6}$ torr) and at low evaporation rates (10-20 Å/sec).

Third, attempts to clean gold substrate for reuse by treatment with chemical reagents (e.g. hot 1:4 $H_2O_2(30\%)/H_2SO_4$) or by plasma cleaning (in oxygen and/or hydrogen plasmas) have not been consistently successful so far. In practice, cleaning the gold substrates for repeated use in monolayer experiments involved additional handling of the substrates that introduce defects; thus,

it was usually more desirable to prepare fresh substrates by evaporation than to clean and reuse them.

Synthesis of Dialkyl Sulfides. The dialkyl sulfides were prepared by two methods, A and B (eq 1). Method A involved preparing n-alkylthioundecanoic acids from 11-mercaptoundecanoic acid and n-alkyl bromides; method B from n-alkanethiols and 11-bromoundecanoic acid. The purity of compounds was established by melting points (<2 $^{\circ}$C in range), satisfactory elemental analysis, and proton NMR spectroscopy. The purity of the carbon numbers, n, for alkyl bromides (n = 9, 10, 12, 13, 14, 16, 17, and 21) used in method A were determined to be 99% or better by gas chromatography (GC). Samples for analysis by GC were prepared by dissolving the bromoalkanes (20 mg) in hexane (10 g) and injecting 2 μL samples using a syringe into a 3% SP2100 column. Intentional doping of 11-n-alkylthioundecanoic acid solution with 1% w/w of an 11-mercaptoundecanoic acid or an alkanethiol indicated that these potential impurities (or their disulfides) severely influenced the observed values of the contact angles. Usually these impurities were easily removed by column chromatography and recrystallization from hexane. The purity of 11-n-alkylthioundecanoic acids was determined to be sufficient when similar results were obtained from methods A and B. The physical properties of the dialkyl sulfides are listed in Table I.

Method A. This general procedure for preparing unsymmetrical dialkyl sulfides is illustrated for 11-methylthioundecanoic acid. To a 100-mL flask containing 50 mL

Table I. Physical Properties of Adsorbates

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$CH_3-S-(CH_2)_{10}CO_2H$	A	43.5-45.0	300 MHz $(CDCl_3)$ 2.47 (t, 2 H) 2.33 (t, 2 H) 2.07 (s, 3 H) 1.60 (m) 1.29 (s)	Calcd for $C_{12}H_{24}SO_2$ C, 62.02; H, 10.41; S, 13.80 Found C, 62.31; H, 10.43; S, 13.88
$CH_3(CH_2)_5-S-(CH_2)_{10}CO_2H$	B	50.5-51.5	250 MHz $(CDCl_3)$ 2.49 (t, 4 H) 2.34 (t, 2 H) 1.58 (m) 1.27 (s) 0.88 (t, 3 H)	Calcd for $C_{17}H_{34}SO_2$ C, 67.50; H, 11.33; S, 10.60 Found C, 67.58; H, 11.53; S, 10.63
$CH_3(CH_2)_9-S-(CH_2)_{10}CO_2H$	A	63.9-64.5	300 MHz $(CDCl_3)$ 2.48 (t, 4 H) 2.33 (t, 2 H) 1.55 (m) 1.31 (s) 0.88 (t, 3 H)	Calcd for $C_{21}H_{42}SO_2$ C, 70.33; H, 11.80; S, 8.94 Found C, 70.58; H, 12.04; S, 9.15
$CH_3(CH_2)_{10}-S-(CH_2)_{10}CO_2H$	A	65.0-65.5	300 MHz $(CDCl_3)$ 2.49 (t, 4 H) 2.34 (t, 2 H) 1.58 (m) 1.30 (s) 0.87 (t, 3 H)	Calcd for $C_{22}H_{44}SO_2$ C, 70.91; H, 11.90; S, 8.60 Found C, 71.05; H, 11.85; S, 8.83
$CH_3(CH_2)_{11}-S-(CH_2)_{10}CO_2H$	B	70.0-71.0	300 MHz $(CDCl_3)$ 2.48 (t, 4 H) 2.33 (t, 2 H) 1.55 (m) 1.24 (m) 0.87 (t, 3 H)	Calcd for $C_{23}H_{46}SO_2$ C, 71.44; H, 11.99; S, 8.29 Found C, 71.68; H, 11.68; S, 8.43

Table I. (Continued)

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$CH_3(CH_2)_{12}-S-(CH_2)_{10}CO_2H$	A	70.5–71.0	300 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.34 (t, 2 H) 1.57 (m) 1.27 (s) 0.87 (t, 3 H)	Calcd for C$_{24}$H$_{48}$SO$_2$ C, 71.94; H, 12.07; S, 8.00 Found C, 72.08; H, 12.29; S, 8.25
$CH_3(CH_2)_{13}-S-(CH_2)_{10}CO_2H$	A	73.7–74.7	300 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.34 (t, 2 H) 1.58 (m) 1.28 (s) 0.87 (t, 3 H)	Calcd for C$_{25}$H$_{50}$SO$_2$ C, 72.40; H, 12.15; S, 7.73 Found C, 72.65; H, 12.00; S, 8.05
$CH_3(CH_2)_{14}-S-(CH_2)_{10}CO_2H$	A	75.0–75.7	300 MHz (CDCl$_3$) 2.48 (t, 4 H) 2.34 (t, 2 H) 1.60 (m) 1.27 (s) 0.88 (t, 3 H)	Calcd for C$_{26}$H$_{52}$SO$_2$ C, 72.83; H, 12.22; S, 7.48 Found C, 73.29; H, 12.23; S, 7.73 and C, 72.84; H, 12.22
$CH_3(CH_2)_{15}-S-(CH_2)_{10}CO_2H$	B	78.5–79.4	300 Mz (CDCl$_3$) 2.48 (t, 4 H) 2.33 (t, 2 H) 1.56 (m) 1.24 (m) 0.87 (t, 3 H)	Calcd for C$_{27}$H$_{54}$SO$_2$ C, 73.24; H, 12.29; S, 7.24 Found C, 73.55; H, 12.45; S, 7.30
$CH_3(CH_2)_{16}-S-(CH_2)_{10}CO_2H$	A	77.5–79.3	250 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.34 (t, 2 H) 1.57 (m) 1.25 (m) 0.86 (t, 3 H)	Calcd for C$_{28}$H$_{56}$SO$_2$ C, 73.62; H, 12.36; S, 7.02 Found C, 73.96; H, 12.45; S, 7.16

Table I. (Continued)

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$CH_3(CH_2)_{17}-S-(CH_2)_{10}CO_2H$	A	79.5–82.0	250 MHz (CDCl$_3$) 2.47 (t, 4 H) 2.33 (t, 2 H) 1.57 (m) 1.23 (s) 0.86 (t, 3 H)	Calcd for $C_{29}H_{56}SO_2$; C, 73.98; H, 12.42; S, 6.81 Found C, 74.02; H, 12.27; S, 7.09
$CH_3(CH_2)_{17}-S-(CH_2)_{10}CO_2H$	B	79.5–81.0	300 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.34 (t, 2 H) 1.57 (m) 1.29 (m) 0.87 (t, 3 H)	Calcd for $C_{29}H_{56}SO_2$; C, 73.98; H, 12.42; S, 6.81 Found C, 74.19; H, 12.45; S, 6.94
$CH_3(CH_2)_{19}-S-(CH_2)_{10}CO_2H$	A	84.0–85.3	250 MHz (CDCl$_3$) 2.48 (t, 4 H) 2.34 (t, 2 H) 1.57 (m) 1.28 (s) 0.88 (t, 3 H)	Calcd for $C_{31}H_{62}SO_2$; C, 74.63; H, 12.53; S, 6.43 Found C, 74.50; H, 12.51; S, 6.55
$CH_3(CH_2)_{21}-S-(CH_2)_{10}CO_2H$	B	88.0–89.5	250 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.34 (t, 2 H) 1.58 (m) 1.24 (s) 0.87 (t, 3 H)	Calcd for $C_{33}H_{66}SO_2$; C, 75.22; H, 12.63; S, 6.08 C, 74.98; H, 12.68; S, 6.31
$CH_3(CH_2)_{15}-S-(CH_2)_{15}CO_2H$	B	85–87	250 MHz (CDCl$_3$) 2.49 (m, broad) 2.33 (t, 2 H) 1.57 (m) 1.23 (s) 0.86 (t, 3 H)	Calcd for $C_{32}H_{64}SO_2$; C, 74.93; H, 12.58; S, 6.25 Found C, 75.10; H, 12.54; S, 6.38

Table I. (Continued)

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$CD_3(CD_2)_{15}-S-(CH_2)_{10}CO_2H$	A	76-78	250 MHz (CDCl$_3$) 2.49 (t, 2 H) 2.36 (t, 2 H) 1.63 (m) 1.32 (m)	
$[CH_3(CH_2)_9]_2S$			250 MHz (CDCl$_3$) 2.50 (t, 4 H) 1.56 (m) 1.26 (m) 0.88 (t, 3 H)	
$[CH_3(CH_2)_{11}]_2S$		40.0-41.5	300 MHz (CDCl$_3$) 2.50 (t, 4 H) 1.57 (m) 1.26 (m) 0.88 (t, 6 H)	Calcd for $C_{24}H_{50}S$ C, 77.76; H, 13.60; S, 8.65 Found C, 78.04; H, 13.70; S, 8.87
$[CH_3(CH_2)_{17}]_2S$		66.5-67.0	300 MHz (CDCl13) 2.49 (t, 4 H) 1.55 (m) 1.27 (m) 0.87 (t, 6 H)	Calcd for $C_{36}H_{74}S$ C, 80.21; H, 13.84; S, 6.21 Found C, 80.03; H, 13.93; S, 6.21
$[CH_3(CH_2)_{21}]_2S$		77.3-78.0	300 MHz (CDCl$_3$) 2.50 (t, 4 H) 1.56 (m) 1.27 (m) 0.89 (t, 3 H)	Calcd for $C_{44}H_{90}S$ C, 81.15; H, 13.93; S, 4.92 Found C, 80.45; H, 13.83; S, 4.73
$[HO_2CCH_2]_2S$		128.5-130.5		Calcd for $C_4H_6SO_4$ C, 32.00; H, 4.03; S, 21.35 Found C, 32.21; H, 3.74; S, 21.71

Table I. (Continued)

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$[HO_2C(CH_2)_2]_2S$		130.0–132.5		Calcd for $C_6H_{10}SO_4$ C, 40.44; H, 5.66; S, 17.99 Found C, 40.60; H, 5.39; S, 18.23
$[HO_2C(CH_2)_5]_2S$		111–112	300 MHz (CDCl$_3$) 2.49 (t, 4 H) 2.35 (t, 4 H) 1.61 (m) 1.43 (m)	Calcd for $C_{12}H_{22}SO_4$ C, 54.94; H, 8.45; S, 12.22 Found C, 44.18; H, 8.73; S, 12.57
$[HO_2C(CH_2)_{10}]_2S$		110.0–111.5	300 MHz (CDCl$_3$) 2.68 (t, 4 H) 2.34 (t, 4 H) 1.64 (m) 1.28 (m)	Calcd for $C_{22}H_{42}SO_4$ C, 65.63; H, 10.51; S, 7.96 Found C, 65.90; H, 10.57; S, 8.16
$[HO_2C(CH_2)_{15}]_2S$		117.5–119	300 MHz (d^{8}THF) 2.46 (t, 4 H) 2.20 (t, 4 H) 1.56 (m) 1.29 (m)	Calcd for $C_{32}H_{62}SO_4$ C, 70.79; H, 11.51; S, 5.91 Found C, 70.82; H, 11.39; S, 5.92
$[HO_2C(CH_2)_{21}]_2S$		117–119	Insoluble	Calcd for $C_{44}H_{86}SO_4$ C, 74.31; H, 12.19; S, 4.51 Found C, 74.39; H, 12.17; S, 4.54
$[HO(CH_2)_{11}]_2S$		84.5–86.0	250 MHz (CDCl$_3$) 3.64 (t, 4 H) 2.50 (t, 4 H) 1.57 (m, 4 H) 1.28 (m, 8 H)	Calcd for $C_{22}H_{46}SO_2$ C, 70.53; H, 12.38; S, 8.56 Found C, 70.80; H, 12.58; S, 8.88

Table I. (Continued)

Compound	Method of Synthesis	mp °C	^{1}H NMR	Analyses
$[CH_3O_2C(CH_2)_{15}]_2S$		78.5-79.5	300 MHz ($CDCl_3$) 3.65 (s, 3 H) 2.48 (t, 4 H) 2.28 (t, 4 H) 1.57 (m) 1.23 (m)	

of methanol (degassed by bubbling argon through the stirred methanol for at least 1 h) was added 11-mercaptoundecanoic acid (500 mg, 2.29 mmol) followed by methyl iodide (325 mg, 2.52 mmol). For longer alkyl chains the bromide was used instead of the iodide. The mixture was stirred under argon and sodium metal (116 mg, 5.04 mg-atom) was added. The resulting solution was clear and homogeneous. The reaction mixture was stirred overnight at room temperature under argon. The product was isolated by pouring the reaction mixture into a beaker containing water (100 mL), conc. HCl (5 mL) and diethyl ether (300 mL). The ethereal layer was separated, extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried with anhyd. sodium sulfate, and filtered. On removal of the ether by rotoevaporation, a white solid was obtained. Recrystallization from hexanes yielded 11-methylthioundecanoic acid.

Method B. This general procedure for preparing unsymmetrical dialkyl sulfides is illustrated for 11-dodecyl-thioundecanoic acid. To a 100-mL flask containing 50 mL of methanol (degassed with argon) was added sodium metal (269 mg, 11.7 mg-atom) followed by dodecanethiol (1.00 mL, 1.18 g, 5.85 mmol). After the thiol had dissolved, 11-bromoundecanoic acid (1.55 g, 5.85 mmol) was added and a clear homogeneous solution formed. After approximately 5 min the sulfide product precipitated from the solution. The reaction mixture was stirred overnight at room temperature under argon to ensure completion. The product was isolated by pouring the reaction mixture into a beaker containing

water (100 mL), conc. HCl (5 mL), and diethyl ether (300 mL). The ethereal layer was separated and extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried with anhydrous sodium sulfate, and filtered. After removal of the ether by rotoevaporation, a white solid was obtained that yielded pure 11-dodecylthioundecanoic acid on recrystallization from hexanes.

11-Mercaptoundecanoic acid. Methanol (250 mL) was added to a 500-mL round-bottomed flask and degassed with argon. Sodium metal (1.73 g, 75.4 mg-atom) was added and allowed to react under an argon atmosphere. The sodium methoxide solution was cooled with an ice-bath, and thiolacetic acid (5.4 mL, 75.4 mmol) was added followed by 11-bromoundecanoic acid (10.0 g, 37.7 mmol). The mixture was heated at reflux for 5 h. and cooled to room temperature with an ice-bath. Degassed 1 N aq. NaOH (150 mL) was added to the reaction flask through a cannula and the mixture was allowed to reflux for 3 h. The reaction was cooled in an ice-bath and poured with stirring into a 1000-mL beaker containing ice-water (200 mL), conc. HCl (35 mL), and diethyl ether (300 mL). The ethereal layer was separated and extracted with deionized water (3 X 100 mL) and with sat. aq. NaCl (150 mL). The ethereal layer was dried over anhydrous sodium sulfate, filtered and the ether removed by rotoevaporation to yield a white solid. After recrystallization from hexanes, 4.5 g (45% yield) of product was recovered.

A number of symmetrical dialkyl sulfides were prepared by reaction of the corresponding alkyl bromides with lithium sulfide.

This procedure is represented by the following:

Di-n-decyl sulfide. To a 100-mL flask containing 50 mL of degassed methanol was added 1-bromodecane (2.00 g, 9.04 mmol) followed by anhydrous lithium sulfide (0.416 g, 9.04 mmol). The reaction mixture was stirred at reflux under argon overnight. The reaction mixture was allowed to cool to room temperature and poured into diethyl ether (200 mL). The ethereal layer was extracted with deionized water (3 X 100 mL), dried over anhydrous sodium sulfate, filtered and rotoevaporated leaving a clear liquid. The liquid product was purified by cold recrystallization from absolute ethanol.

Di-n-docosyl sulfide. 22-Bromodocosane (5 g, 2.8 mmol) was dissolved in 20 mL of chloroform. A solution of anhydrous lithium sulfide (0.91 g, 19.8 mmol) and trimethylhexadecylammonium bromide (20 mg) in 3 mL of water was added to the bromide and the resulting two-phase mixture stirred at reflux for 8 h. A white solid precipitated as the solution was cooled to room temperature. The solid was collected by filtration and dried in vacuo to give 3.4 g (80%) of didocosyl sulfide. The product was recrystallized twice from hot ethanol to give shiny white leaflets.

Formation of Self-Assembled Monolayers. Generally, monolayer films were prepared by the immersion of gold substrates using Teflon-coated tweezers into precleaned 20-mL glass bottles that contained approximately 15 mL of an unstirred solution (e.g. 0.01 to 0.1% weight dialkyl sulfide in ethanol) at ambient temperature (usually 20-25 $^{\circ}$C) for 12 to 36 h. Afterwards, the

films were washed by rinsing both sides of the coated substrate three times with an appropriate solvent (e.g. 1 mL of ethanol) using a disposable glass pipette equipped with a rubber bulb, and then dried in a stream of argon for 5-15 seconds. The properties of the films were measured immediately by ellipsometry and contact angle goniometry. Gold substrates were prepared and treated by standard procedures that are described further in the section concerned with the preparation of gold substrates and used immediately after they were washed with ethanol. Glass weighing bottles that were used for adsorption were cleaned either by filling and emptying the bottles three times each with methylene chloride, deionized water, ethanol, and pure adsorption solvent, or by immersion of the weighing bottles in a glass container containing a solution of 1:4 H_2O_2 (30%)/H_2SO_4 (conc.) at 80 ^oC for 1 h followed by filling and emptying the bottles three times each with water, ethanol, and pure adsorption solvent. The latter procedure was always employed if the glassware had previously been exposed to thiols. Glass bottles were handled using Teflon-coated tweezers during the cleaning procedure and allowed to drain and dry on a wooden rack. Adsorption solutions were prepared by weighing a few mg of sulfide and approximately 15 g of pure solvent into a pre-cleaned 20-mL glass weighing bottle. Most of the monolayer films in this study were generated by self-assembly from solutions within 1-4 h of preparation. Monolayer films of similar quality could be prepared using adsorption solutions up to several weeks old. After several h of adsorption, the monolayer films had

attained their limiting properties (Figure 7). In addition, the properties of representative films prepared by adsorption from THF for 24 h and 10 days were similar (Table II). The susceptibility of ethanolic solutions of mercaptoalkanoic acids to oxidation was checked after two weeks by ^{1}H NMR and indicated that less than 3% of the mercaptoalkanoic acid had oxidized to the disulfide. Occasionally, adsorption solutions were prepared using degassed ethanol, methanol, hexane, or hexadecane with results similiar to those obtained using undegassed solvents. Many dialkyl sulfides of high molecular weight were not soluble in ethanol at concentrations of 0.01 to 0.1%. Nonetheless, good quality monolayer films were formed by self-assembly from the saturated solutions containing suspended solids. The properties of monolayer films prepared using other solvents for adsorption are similar (Table III). Monolayer films did not seem to be affected by the washing procedure. For instance, a monolayer film of didocosyl sulfide onto gold was washed with ethanol 10 times and then sonicated in pure ethanol for 10 min with no changes observed in the thickness or contact angles (Table IV).

Contact Angle Measurements. Contact angles were determined on sessile drops using a Rame-Hart Model 100 contact angle goniometer, equipped with a controlled environment chamber, by estimating the tangent to the drop at its intersection with the surface. These were determined 5-20 sec after application of the drop to the surface. The relative humidity in the chamber was maintained at 100% by filling the wells in the sample chamber with

Table II. Values of Contact Angle (Deionized Water, pH = 5.6) on Representative Films Prepared by Adsorption for 24 Hours and 10 Days from Tetrahydrofuran.

Compound	θ_a (24 h)	θ_a (10 days)
$S[(CH_2)_{10}CO_2H]_2$	41	52
$CH_3(CH_2)_nS(CH_2)_{10}CO_2H$		
n = 0	41	36
n = 9	83	80
n = 16	89 91	88
n = 21	99 99	100
$S[(CH_2)_{21}CH_3]_2$	110	113

Table III. Properties of Representative Films Prepared by Adsorption from Selected Solvents.

Compound	Ethanol Thickness (Å)	θ_a	Tetrahydrofuran Thickness (Å)	θ_a	Hexadecane Thickness (Å)	θ_a
$S[(CH_2)_{10}CO_2H]_2$	12	48[b],66[c]	-	41[b]	11[a]	58[c]
	8	48[b],61[c]	-	-	11[a]	-
	12	36[b],54[c]	-	-	-	-
	-	45[b]	-	-	-	-
$CH_3(CH_2)_nS(CH_2)_{10}CO_2H$						
n = 0	8	45[b]	-	41[b]	-	-
	10	52[b]	-	-	-	-
n = 9	7	78[c]	-	83[b]	-	-
n = 16	8[a]	92[c]	-	89[b]	-	-
	6[a]	90[c]	-	91[b]	-	-
n = 21	8[a]	94[c]	-	99[b]	-	-
$S[(CH_2)_{21}CH_3]_2$	25[a]	111[c],46[d]	24	110[b],46[d]	28[a]	112[c],45[d]

[a] Adsorption from saturated solutions
[b] Values of contact angle (deionized water, pH = 5.6) measured before ellipsometry experiments.
[c] Values of contact angle (deionized water, pH = 5.6) measured after ellipsometry experiments.
[d] Values of contact angle (hexadecane)

Table IV.   Effect of Washing with Ethanol Films Prepared by
Adsorption from 0.1% Didocosyl Sulfide in
Tetrahydrofuran for 3 Hours.

Times Washed	Thickness Å	$\theta_a(H_2O)$ [b]	$\theta_a(HD)$ [c]
0 [a]	25	111	46
1	24	110	46
2	25	110	46
3	25	110	45
4	24	109	45
6	24	109	45
10	23	110	45
(Sonification for 10 min. in 15 mL EtOH)	23	110	45

[a]Measurements were made immediately after the slide had been
removed from adsorbate solution.

[b]Contact angle (deionized H_2O, pH = 5.6).

[c]Contact angle (hexadecane).

distilled water. The temperature was not controlled and varied

between 20 and 25 $^{\circ}$C. The volume of the drop used was 5 μL; values

of contact angle were, however, independent of the volume of the

sessile drops in the range 1 to 20 μL. The samples were prepared

and handled with Teflon-coated tweezers as described for the

formation of monolayer films. All reported values are the average

of at least six measurements taken at different locations

(separated by at least 1 cm) on the film surface and have a maximum

range of ±3°. Sessile drops for both advancing and receding

contact angles were applied with a syringe using the technique

described by Dettre and Johnson.[68] Sessile drops for advancing

angles were formed with a syringe by allowing the drops to contact

the surface and increasing the volume of the drop to 5 μL while

withdrawing the syringe. Sessile drops for receding angles were

formed by applying a 10-μL drop to the surface and then reducing

the volume of the drop by removing liquid with a syringe (removed

approximately 5 μL) until the periphery of the drop retreated.

Measurements of receding angle were taken within 5-20 s after

formation of the sessile drop. Values of receding contact angle

are shown in Figure 14. Values of advancing contact angle for

several representative films were measured as a function of time

after application (Figure 15) and for films before and after

immersion in deionized water for several days (Table V). In both

instances, no significant change was observed.

Ellipsometry measurements. Ellipsometry measurements

were made with a Ruldolph Research Type 43603-200E Thin Film
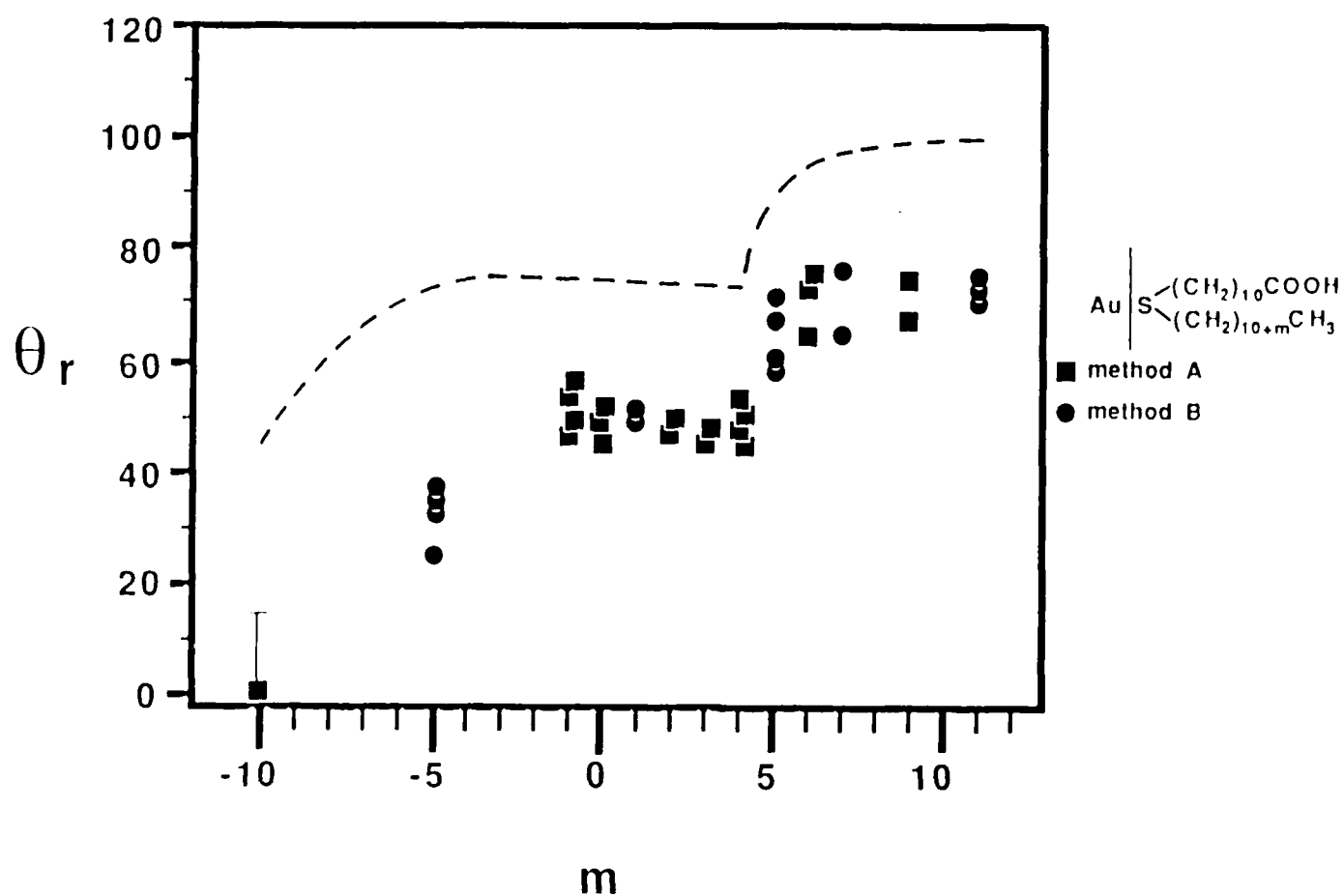
Figure 14. Receding contact angles (deionized water, pH = 5.6) for monolayer surfaces prepared from 11-n-alkylthioundecanoic acids adsorbed onto gold. Solid squares represent adsorbates prepared by method A and solid circles those prepared by method B. The dashed line is a best fit to the advancing angles presented in Figure 10.
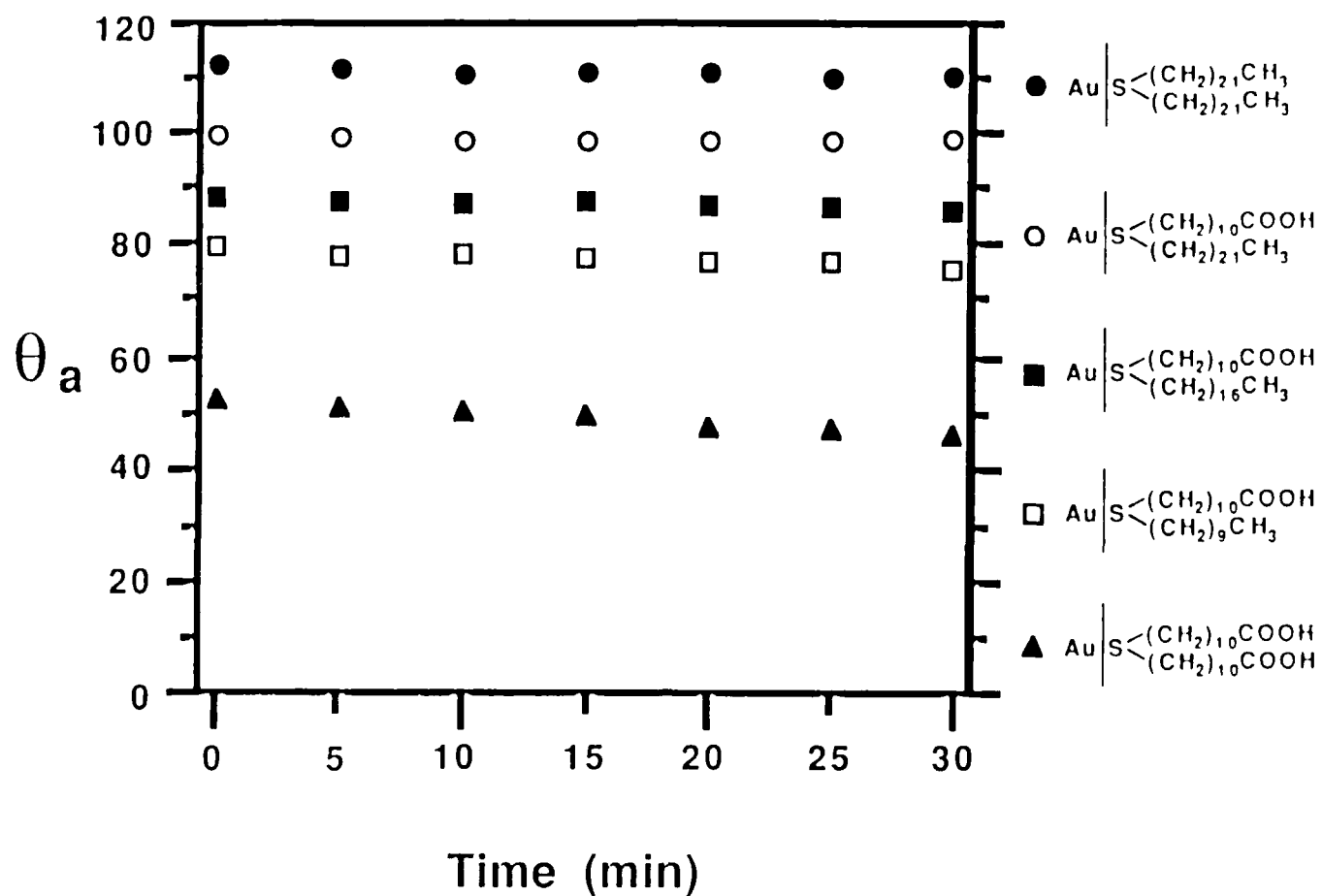
Figure 15. Stability of advancing contact angles (deionized water, pH = 5.6) for representative films prepared by adsorption from tetrahydrofuran as a function of time after application of the drops in goniometer chamber (100% humidity).

Table V.   Contact Angles of Water (pH = 5.6) on Monolayer Films
            Before and After Soaking Under Water for 2 Days.

Compound	θ_a (Initial)	θ_a (Final)
$S[(CH_2)_{10}CO_2H]_2$	52	51
$CH_3(CH_2)_nS(CH_2)_{10}CO_2H$		
n = 5	78	76
n = 9	82	77
n = 16	93	91
n = 17	98	93
$S[(CH_2)_{21}CH_3]_2$	112	111 (3 days)

Ellipsometer equipped with a He-Ne laser light source (6328 Å).
The angle of incidence was 70.0° and the compensator was set at
-45.0°. Further details concerning ellipsometry experiments have
been described previously by Allara and Nuzzo.[19] Measurements
necessary for the calculation of the film thickness consisted of
the determination of two sets of polarizer and analyzer readings
(averaged values of P1, A1, P3, and A3) for the "bare" gold
substrate and the corresponding set of values for the substrate
coated with a monolayer film.

Values for each set of polarizer and analyzer settings,
measured in zone 1 (P1 and A1) and zone 3 (P3 and A3), are the
average of at least three measurements taken at different locations
(separated by at least one cm) on the sample and had a maximum
scatter of ±0.15°. These measurements were determined with the
sample exposed to air and within 10 min after the samples had been
washed with ethanol. After the determination of the set of values
(P1, A1, P3, and A3) for a "bare" gold substrate, the substrate was
washed with ethanol and immersed immediately in the solution of the
adsorbate. The freshly prepared monolayers were washed with
ethanol and the corresponding set of values (P'1, A'1, P'3, and
A'3) were determined for the monolayer films. A chart of values of
thickness and p (where $p = P'1 + P'3 - 90°)/2$ and the phase shift
(Δ) upon reflection is given by $2p + 90°$) was generated with a
computer program based on the algorithm of McCracken[50] using the
averaged sets of values for P1, A1, P3, and A3 for the bare
substrates and optical constants for the films of $n_f = 1.45$ and

$k_f = 0$. Values of thickness for the films were determined by
comparisons of the observed average values of p to the
corresponding calculated values of p and thickness.

X-Ray Photoelectron Spectroscopy. The XPS data in Table
VI were determined using a Physical Electronics Model 548
spectrometer (Mg K_α X-ray source, cylindrical mirror analyzer, 50
eV pass energy; 10^{-8} to 10^{-9} torr) calibrated according to ASTM STP
699. Samples for XPS analysis were from electron-beam evaporated
gold substrates using procedures already described. Samples were
cut into 1-cm X 1-cm squares using a diamond-tipped cutter, washed
with ethanol and introduced into the spectrometer. For each sample
a survey spectrum and high resolution spectra of the C 1s, O 1s,
S 2p, and Au 4f were collected. The peak areas obtained from the
multiplex routine were converted to atomic concentrations using the
following sensitivity factors: C 1s - 0.250; O 1s - 0.60; S 2p -
0.54; Au 4f 7/2 - 2.8. These atomic percentages are reported in
the first line of each entry in Table VI. The composition was then
recalculated omitting gold from calculations as shown in the second
line of each entry. The third line indicates the expected
monolayer composition calculated on the assumption, among others,
that the monolayer is isotropic and that the escape depth is
independent of electron energy. Comparing the bottom two lines we
see that the values for sulfur are consistently low and the values
for oxygen are consistently high - the predicted behavior for
sulfur atoms at the gold-oxygen interface and oxygen atoms near the
exterior of the monolayer.

Table VI. Atomic Concentrations of Representative Films Estimated by XPS.

Compound	%Au	%C	%S	%O
CH_3-S-$(CH_2)_{10}CO_2H$				
Observed for Au, C, S, O	32.3	54.9	3.0	9.8
Observed, for C, S, O		81.1	4.4	14.5
Calcd for $C_{12}SO_2$		80.0	6.7	13.3
$CH_3(CH_2)_5$-S-$(CH_2)_{10}CO_2H$				
Observed for Au, C, S, O	37.7	52.2	1.5	8.6
Observed for C, S, O		83.8	2.4	13.8
Calcd for $C_{17}SO_2$		85.0	5.0	10.0
$CH_3(CH_2)_{12}$-S-$(CH_2)_{10}CO_2H$				
Observed for Au, C, S, O	29.0	55.9	2.5	12.7
Observed for C, S, O		78.6	3.5	17.9
Calcd for $C_{24}SO_2$		88.9	3.7	7.4
$CH_3(CH_2)_{19}$-S-$(CH_2)_{10}CO_2H$				
Observed for Au, C, S, O	33.1	58.7	1.2	7.0
Observed for C, S, O		87.7	1.8	10.5
Calcd for $C_{31}SO_2$		91.2	2.9	5.9
$HS(CH_2)_{11}CH_3$				
Observed for Au, C, S, O	35.9	61.7	2.3	0.1
Observed for C, S, O		96.3	3.6	0.2
Calcd for $C_{12}S$		92.3	7.7	0.0
$HS(CH_2)_{10}CO_2H$				
Observed for Au, C, S, O	21.5	58.9	2.2	17.5
Observed for C, S, O		74.9	2.8	22.3
Calcd for $C_{11}SO_2$		78.6	7.1	14.3

The XPS spectra in Figure 8 were obtained on a modified Kratos XSAM-800 Photoelectron Spectrometer operated in a Fixed Analyzer Transmission mode and with an instrumental resolution of about 1.1 eV. The base pressure of the spectrometer was less than 5×10^{-11} torr. All spectra were collected using a Mg K_α excitation (1253.6 eV). Due to the observed sensitivity of these samples to desorption and/or decomposition processes originating from the secondary electron emission, the X-ray flux was reduced to a very low level (12 KeV, 2mA) and the samples cooled to about -100 $^\circ$C in the UHV chamber. The binding energies were referenced to Au 4f 7/2 at 84.0 eV. Samples were prepared as described previously for the formation of monolayer films with the exception that the freshly evaporated gold substrates (prepared using the AT&T evaporator) were directly immersed into adsorbate solutions without washing with ethanol beforehand.

Infrared Spectroscopy. Infrared spectra were obtained by reflection of a p-polarized beam from the gold surface at the near-glancing angle of incidence of 86°. More complete details of the equipment and procedure are given elsewhere[19] but a brief description is given here. The instrumentation consisted of a modified Digilab 15B Fourier transform spectrometer system equipped with a liquid nitrogen cooled MCT narrow band detector and operating at a resolution of 2 cm^{-1}. Each absorption spectrum was referenced to an unreacted gold substrate which had been cleaned immediately prior to measurement in order to remove adsorbed organic impurities. The samples were mounted in a box, purged with

purified nitrogen gas and isolated from the spectrometer by a KBr

window. This procedure was necessary to minimize adsorption of

water and other polar materials onto films that had exposed polar

groups. Samples were prepared by the immersion of gold substrates

(prepared using a modified Varian evaporator at AT&T Laboratories)

into adsorption solutions (0.1% adsorbate in ethanol) for 24 hours

as described previously.

Scanning Electron Microscopy. SEM micrographs were

obtained on a JEOL JSM35 Scanning Electron Microscope using a 35 kV

accelerating potential and a sample tilt of 30°, at magnifications

up to ( ),000X. The microscope was focused on a speck of dust or a

gold colloid deposited for this purpose, moved to a blank area of

the sample, and the micrograph taken "blind." If the SEM was very

well aligned and focused, low rolling hills a few hundred ångstroms

across were resolved at a magnification of 60,000X.

Kinetics of Formation of Monolayers. Formation of

monolayer films was monitored conveniently by ellipsometry and

contact angle measurements (Figure 7). Gold substrates (prepared

using Prof. Klemperer's evaporator) and films were prepared in

accordance with general procedures described previously. The

experiment was carried out by making repeated measurements of

contact angle (deionized water, pH 5.6) and thickness (by

ellipsometry) on individual gold substrates that were immersed

repeatedly for different times of adsorption. Samples were removed

from adsorption solutions and washed with ethanol. After

measurement of contact angle, the samples were washed with

deionized water, washed with ethanol, and the thickness measured by ellipsometry. The samples were then washed with ethanol and reimmersed in the adsorption solutions.

Interfacial Reconstruction. Experiments in Figure 12 were carried out as described below. Gold substrates (prepared using the Varian evaporator at AT&T Bell Laboratories) and films were prepared in accordance with the general procedures described previously. Three samples were prepared by the immersion of three gold substrates into an 0.1% ethanolic solution of bis-(11-carboxyundecyl)sulfide for 24 h. Values of contact angle for buffers ranging from pH of 1 up to pH of 9 were stable for at least 2 min after application of the drop to the surface. Values of contact angle measured with buffers at pH 10 and pH 11 on the film exposed to argon decreased with time and reached limiting values of 10 to 20 degrees in a few minutes. (The reported values at θ_a at pH of 10 and 11 were measured within 5-20 sec after application of the buffers.) Similar contact angle behavior was observed for other monolayer films (Tables VII and VIII).

Thermal reconstruction. A sample for the thermal reconstruction experiment was prepared by immersing a gold substrate (prepared using Prof. Klemperer's evaporator) into a 0.1% ethanolic solution of bis-(11-carboxyundecyl)sulfide for 24 h. Afterwards, the film was removed from the adsorption solution and washed with ethanol. The measured thickness was 12 Å and the water (pH = 5.6) contact angles were 39° and 48° before and after the ellipsometric measurements were made, respectively. The sample was

Table VII. Effect of Variation of pH on Contact Angles.

Compound	$\theta_a(pH=5.6)$	$\theta_a(pH=13)$[a]	$\Delta\theta_a(pH=5.6-pH=13)$[a]
$S[(CH_2)_{21}CH_3]_2$	113	112[b]	1
$CH_3(CH_2)_nS(CH_2)_{10}CO_2H$			
n = 21	97	80	17
n = 19	96	78	18
n = 17	94[c]	85[c]	9[c]
n = 16	91	83	8
n = 14	76	65	11
n = 10	78	70	8
n = 9	80	65	15
n = 5	76	62	14
n = 0	48	23	25
$S[(CH_2)_{10}CO_2H]_2$	44	8	36

[a]Monolayer films of dialkyl sulfides are not stable to 0.1 NaOH solution. Initial contact angles are reported within 1 min of application of test drops.

[b]Contact angle values for both acidic and basic drops were reproducible if the monolayer was in contact with 0.1 N NaOH solution for less than 1 min.

[c]After exposure to drops of 0.1 N NaOH, θ_a for 0.1 N HCl decrease from 94° to 87° and θ_a for 0.1 N NaOH decreased from 85° to 66°.

Table VIII. Contact Angles of Water (pH = 5.6) for Monolayer Films Subsequently Exposed to Various Media for 2 Days.

Compound	θ_1 (Initial)	θ_2 (Air/Ar)	θ_3 (H_2O/EtOH)	θ_4 (Air/Ar)	θ_5 (H_2O)
$S[(CH_2)_{10}CO_2H]_2$	44°	55°	41°a	54°	41°
	48	61	46	--	--
	48	66b	53a	70	65
	45	56	58a	65	52
$CH_3S(CH_2)_{10}CO_2H$	46	65c			
	48d	58			
	48	57			

a θ_a was less than 15 degrees initially but increased on exposure to air before contact angle measurements could be made (i.e. within 15 s).

b Basic drops were not stable. θ_a decreased and the drop periphery spread with time. θ_a (pH = 13) = 41°, (32°, 5 min), (28°, 10 min).

c Basic drops were not stable. θ_a decreased and the drop periphery spread with time. θ_a (pH = 13) = 46°, (41°, 1 min), 36°, 5 min), (31°, 10 min), (28°, overnight).

d θ_a (pH = 13) = 38°, (28°, 2 min), (23°, 5 min).

then washed with water and ethanol and stored in a glass container filled with argon at 80 °C for 1 h. Directly after this treatment, the measured contact angle has risen to 54° and the thickness had decreased to 8 Å.

Supplementary Material: Further details of preparation of dialkyl sulfides not described above may be found in supplemental material to this journal. Ordering information can be found on any current masthead.

Notes and References

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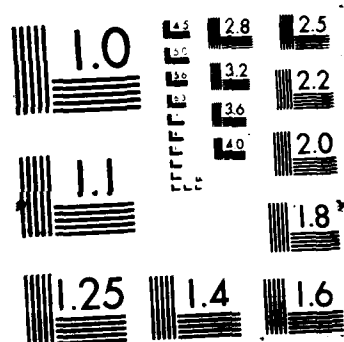
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Captions

Figure 1.   Schematic illustration of the physical-organic approach to the design of interfaces with "buried" functionality. The alkyl chains are indicated here as extended only for illustration; they are almost certainly less ordered than these diagrams suggest.

Figure 2.   Scanning electron micrograph of a gold sample representative of those used in these studies. A 100-nm bar is shown.

Figure 3.   Schematic illustration of the influence of a small plateau on the interface presented by $S[(CH_2)_nCO_2H]_2$.

Figure 4.   Values of contact angle (deionized water, pH = 5.6) for representative films as a function of chain length.

Figure 5.   Measurement of film thickness (by ellipsometry) and contact angle (deionized water, pH = 5.6) for representative films. Values of thickness and contact angle were obtained close to one another, but not necessarily at exactly the same location. All points having the same symbol were obtained using one sample. The data for $CH_3(CH_2)_{21}S(CH_2)_{10}CO_2H$ are representative of data showing an _unacceptable_ level of reproducibility (presumably due to contamination of the surface at some point during the preparation of the film); data for other compounds show scatter that we considered normal and acceptable.

Figure 6. Film thickness (by ellipsometry) of representative films as a function of chain length.

Figure 7. Kinetics of formation of representative films. The upper graph is a plot of thickness (by ellipsometry) as a function of time of adsorption. The lower graph is a plot of contact angle (deionized water, pH = 5.6, unless otherwise specified) as a function of time of adsorption. Values of contact angle at pH 11 were measured with 0.05 M Na_2HPO_4 phosphate buffer. The asterisks represent values for all samples before exposure to the solution containing the organosulfur compound.

Figure 8. X-ray photoelectron spectra for representative films adsorbed onto gold. Left, Survey XPS spectra. Right, Spectra of the C 1s region. The signals at 288.8 eV are attributed to carboxylic acid groups and at 284.7 eV to the carbon atoms of the alkyl chains.

Figure 9.   Polarized infrared external reflection spectra of
representative films prepared by spontaneous assembly
of diundecylsulfide bis-(11-carboxyundecyl)sulfide,
11-methylthioundecanoic acid, and 11-hexadecyl-d_{33}-
thioundecanoic acid adsorbates from dilute ethanol
solutions onto gold. Signals at 2925 cm^{-1} and 2923 cm^{-1}
are attributed to the CH$_2$ asymmetric stretch, those at
2853 cm^{-1} and 2860 cm^{-1} to the CH$_2$ symmetric stretch
those at 1740 cm^{-1} and 1717 cm^{-1} to the C=O stretch,
and those at 2196 cm^{-1} and 2095 cm^{-1} to the CD$_2$
asymmetric stretch and CD$_2$ symmetric stretch
respectively. Other peaks are not interpreted in
detail but correspond roughly to those observed in pure
compounds. Note the absence of an observable C=O
stretch in the spectrum of the film prepared from
11-hexadecyl-d_{33}-thioundecanoic acid, even though
signals attributable to the methylene and
deuterium-labeled methylene chains are observed.n
Scale bars in absorbance units are provided for the
high and low frequency spectra of the deuterated
sulfide.

Figure 10. Advancing contact angles (deionized water, pH = 5.6) for monolayer surfaces prepared from 11-n-alkylthioundecanoic acids, adsorbed onto gold. Solid squares represent adsorbates prepared by method A and solid circles those prepared by method B (eq 1). Open symbols represent values for the interfaces presented by symmetrical dialkylsulfides adsorbed onto gold, and are included for reference.

Figure 11. Advancing contact angles of selected aqueous buffers for monolayer surfaces prepared from didocosyl sulfide, 11-n-docosylthioundecanoic acid. 11-n-eicosylthio-undecanoic acid, 11-n-octadecylthioundecanoic acid, 11-n-decylthioundecanoic acid, and bis-(11-carboxy-undecyl) sulfide adsorbed onto gold. Contact angles were measured within 1 minute and are not necessarily equilibrium values.

Figure 12. Effect of exposure to air on the advancing contact angles of selected aqueous buffers for monolayer surfaces prepared from di(11-carboxyundecyl) sulfide adsorbed onto gold.

Figure 13. Schematic illustration of the influence of the ordering of films on the interfaces presented by perfectly ordered films (A) and the loosely ordered sulfide films in this study (B).

Figure 14. Receding contact angles (deionized water, pH = 5.6) for
            monolayer surfaces prepared from
            11-n-alkylthioundecanoic acids adsorbed onto gold.
            Solid squares represent adsorbates prepared by method A
            and solid circles those prepared by method B.   The
            dashed line is a best fit to the advancing angles
            presented in Figure 10.

Figure 15. Stability of advancing contact angles (deionized water,
            pH = 5.6) for representative films prepared by
            adsorption from tetrahydrofuran as a function of time
            after application of the drops in goniometer chamber
            (100% humidity).

Monolayer Films Prepared by the Spontaneous Self-Assembly of Symmetrical and Unsymmetrical Dialkyl Sulfides from Solution onto Gold Substrates: Structure, Properties, and Reactivity of Constituent Functional Groups[1]

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General. Physical constants for all compounds described here are given in Table I in the journal text.

11-Methylthioundecanoic acid was prepared using the procedure of method A. The product was purified by passing through a column containing silica gel using a solution of acetone-hexane (1/10). Removal of the eluent by rotoevaporation afforded a white solid.

11-Hexylthioundecanoic acid was prepared as described in method B using 1-hexanethiol (1.00 g, 8.46 mmol), 11-bromoundecanoic acid (2.24 g 8.46 mmol), and sodium metal (428 mg, 18.6 mg-atom) in degassed methanol. The product was recrystallized from hexanes. The product was purified by passing through a column containing silica gel with a solution of acetone-hexane (1/5), collecting 50- mL fractions. Recrystallization of the product from hexanes afforded a white solid.

11-Decylthioundecanoic acid was prepared as described in method A using 1-bromodecane (1.02 g, 4.61 mmol), sodium metal (193 mg, 8.38 mg-atom), and 11-mercaptoundecanoic acid (0.915 g, 4.19 mmol) in degassed methanol. The product was recrystallized from hexanes and purified by passing a solution in acetone-hexane (1/9) through a column containing silica gel. Concentration of the eluent by rotoevaporation followed by recrystallization from hexanes afforded a white solid.

11-Undecylthioundecanoic acid was prepared as described in method A using 1-bromoundecane (1.08 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recystallization from hexane afforded a white solid.

11-Dodecylthioundecanoic acid was prepared exactly as described in method B. Recrystallization from hexanes afforded a white solid.

11-Tridecylthioundecanoic acid was prepared as described by method A using 1-bromotridecane (1.21 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Tetradecylthioundecanoic acid was prepared as described by method A using 1-bromotetradecane (1.27 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Pentadecylthioundecanoic acid was prepared as described in method A using 1-bromopentadecane (1.34 g, 4.59 mmol), sodium metal (211 mg, 9.18 mg-atom), and 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol) in degassed methanol. Recrystallization from hexane afforded a white solid.

11-Hexadecylthioundecanoic acid was prepared as described in method B using 1-hexadecanethiol (1.00 g, 3.87 mmol), sodium metal (178 mg, 7.74 mg-atom), and 11-bromoundecanoic acid (1.03 g, 3.87 mmol) in degassed methanol. Recrystallization from hexanes afforded a white solid.

11-Heptadecylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (0.500 g, 2.29 mmol), 1-bromoheptadecane (0.733 g, 2.29 mmol), and sodium metal (105 mg, 4.59 mg-atom). The product was recrystallized from hexanes and then passed through a column of silica gel with a solution of ethylacetate-hexanes (25/75). After chromatography,

the product was recrystallized from hexanes to afford a white solid.

1-Bromoheptadecane was prepared by the addition of 1-heptadecanol (10 g, 39 mmol) to a 250-mL round-bottomed flask. Acetic acid (50 mL) and 48% hydrobromic acid (50 mL) were added to the reaction flask and the mixture was refluxed for 72 h. The mixture was cooled to room temperature and hexanes (250 mL) were added to the mixture. The hexanes layer was separated and extracted with saturated aqueous sodium chloride (3 X 100 mL), dried over anhydrous sodium sulfate, and filtered. The bromide was separated easily from the starting alcohol by filtration through silica gel followed by rinsing the silica gel with hexanes (150 mL). Removal of the hexanes by rotoevaporation afforded a white solid: mp 29-31 °C.

11-Octadecylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (1.00 g, 9.16 mmol), 1-bromooctadecane (1.53 g, 4.58 mmol), and sodium metal (211 mg, 9.16 mg-atom). The product was recrystallized from hexanes and passed through a column of silica gel with a solution of ethyl acetate-chloroform (1/9) collecting 50 mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid. 11-Octadecylthioundecanoic acid was also prepared as described in method B using octadecanethiol (1.00 g, 3.49 mmol), sodium metal (160.5 mg, 6.98 mg-atom), and 11-bromoundecanoic acid (0.925 g, 3.49) in methanol. The product was recrystallized from hexanes and

passed through a column of silica gel (R_f = 0.4) with a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid.

11-Eicosylthioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (1.00 g, 4.59 mmol), 1-bromoeicosane (1.66 g, 4.59 mmol,), and sodium metal (211 mg, 9.18 mg-atom) in methanol. The addition of 50 mL of chloroform to the ethereal layer was necessary to improve solubility during work-up. The product was recrystallized from hexanes and passed through a column of silica gel (R_f= 0.5) with a solution of ethyl acetate-chloroform (1/9), collecting 50 mL fractions. Removal of the eluent by rotoevaporation followed by recrystallization from hexanes afforded a white solid.

11-Docosylthioundecanoic acid was prepared as described in method B from 1-docosanethiol (1.00g, 2.92 mmol), 11-bromoundecanoic acid (0.77 g, 2.92 mmol), and sodium metal (246 mg, 10.7 mg-atom) in methanol. The addition of chloroform to the ethereal layer was necessary to improve solubility during work-up. The product was recrystallized from hexanes (mp 87.5-89.0 °C) and passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9) and collecting 50 mL fractions. Removal of the eluent by rotoevaporation from fractions 5-12 followed by recrystallization from hexanes afforded a white solid. Docosanethiol was prepared by mixing 1-bromodocosane (18 g, 46.2 mmol), thiolacetic acid (6.6 mL, 92.4 mmol), and sodium metal

(2.12 g, 92.4 mg-atom) in a 500-mL round-bottomed flask containing 250 mL of degassed ethanol. The reaction mixture was refluxed under argon for 5 h. After cooling to room temperature, conc. HCl (25 mL) was added to the reaction vessel and the mixture was refluxed overnight. The thiol was purified by recrystallization from hexane to yield a white solid: mp 46-48 °C; 300 MHz ^{1}H NMR (CDCl$_3$) δ 2.52 (q, 2 H); 1.61 (m); 1.25 (m).

16-Hexadecylthiohexadecanoic acid. 16-Bromohexadecanoic acid was prepared by refluxing a mixture of 16-hydroxyhexadecanoic acid (15 g), 48% hydrobromic acid (75 mL), and glacial acetic acid (75 mL) in a 500-mL round-bottomed flask for 2 days. After cooling the reaction mixture to room temperature, the bromide was isolated by filtration using a Buchner funnel and the product was rinsed with deionized water to remove excess hydrobromic acid and acetic acid. The product was recrystallized from hexanes: mp 68.5-70.3 °C; 300 MHz ^{1}H NMR (CDCl$_3$) δ 3.39 (t, 2 H), 2.34 (t, 2 H), 1.84 (m, 2 H), 1.63 (m), 1.27 (m). To a 500 mL round-bottomed flask were added 16-bromohexadecanoic acid (5 g, 14.9 mmol), anhydrous methanol (250 mL), and concentrated sulfuric acid (3 mL). The reaction mixture was refluxed 24 hours. After cooling to room temperature, diethyl ether (300 mL) was added followed by the addition of enough water to form two phases. The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl solution (100 mL). The ethereal layer was dried with anhydrous sodium sulfate, filtered, and the ether was removed by rotoevaporation to afford a slightly yellow residue. Purification

of methyl 16-bromo- hexadecanoate (4 g) was accomplished by flash chromatography using silica gel and ether-hexanes (1/9) as the eluent, collecting 125-mL fractions. The product was recovered by rotoevaporation of fractions 5-8. After recrystallization from hexanes, white crystals were recovered.

16-Hexadecyl-thiohexadecanoic acid was prepared as described in method B using hexadecanethiol (0.37 g, 1.43 mmol), methyl 16-bromohexadecanoate (0.5 g, 1.43 mmol), sodium metal (250 mg, 10.9 mg-atom), and degassed ethanol as the solvent. The ester was isolated by the addition of diethyl ether (300 mL), water (200 mL), and concentrated hydrochloric acid (5 mL) to the reaction mixture. The ethereal layer was separated and extracted with water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. Removal of the ether by rotoevaporation afforded a white solid. The ester was hydrolyzed by refluxing in a solution of THF (100 mL), water (100 mL), and concentrated hydrochloric acid (5 mL) for 4 days. The product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. The solid residue was rinsed with water using suction filtration, dried, and recrystallized from THF, affording a white solid: mp 84-86 $^{\circ}$C. The product was passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent from fractions 4-10 followed by recrystallization for hexanes afforded a white solid.

11-Hexadecyl-d_{33}-thioundecanoic acid was prepared as described in method A using 11-mercaptoundecanoic acid (0.310 g, 1.42 mmol) and d_{33}-bromohexadecane (0.50 g, 1.48 mmol). The product was recrystallized from hexanes and passed through a column of silica gel using a solution of ethyl acetate-chloroform (1/9), collecting 50-mL fractions. Removal of the eluent by rotoevaporation from fractions 5-11 followed by recrystallization from hexane afforded a white solid.

Di-n-dodecyl sulfide. To a 100-mL round-bottomed flask containing 50 mL of degassed ethanol were added 1-bromododecane (1.23 g, 4.94 mmol), dodecanethiol (1.0 g, 4.94 mmol.) and sodium metal (228 mg, 9.92 mg-atom). The reaction mixture was stirred at room temperature under argon for 18 h. The mixture was worked up by extraction with ether. The product was purified by repeated recrystallization from ethanol.

Bis-(1-carboxymethyl)sulfide was obtained from Aldrich and was recrystallized from deionized water to afford a white crystalline solid.

Bis-(2-carboxyethyl)sulfide was obtained from Aldrich and was recrystallized from deionized water to afford a white crystalline solid.

Bis-(6-carboxyhexyl)sulfide was prepared by dissolving methyl-6-iodohexanoate[1] (5.6 g, 22 mmol) in 50 mL of anhydrous methanol (degassed by bubbling argon through the liquid with stirring for at least 1 h) in a 250-mL round-bottomed flask. Lithium sulfide (0.5 g, 11 mmol) was added and the reaction mixture

stirred overnight under argon. The reaction was poured, with stirring, into a 500-mL beaker containing diethyl ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL), and sat aq NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a colorless liquid. The liquid (bis-(6-carbomethoxyhexyl)sulfide) was hydrolyzed by adding the ester to a 250 mL round-bottomed flask containing degassed 1 N aqueous NaOH (25 mL, 25 mmol) and degassed methanol (50 mL). After refluxing for 5 h, the product was isolated by neutralizing with cold, dilute HCl and extracting with ether. The ethereal layer was extracted with deionized water (3 X 100 mL), dried over anhydrous sodium sulfate, and filtered. After removal of the ether, a white solid was recovered. Recrystallization from deionized water gave white crystals.

Bis-(11-carboxyundecyl)sulfide was prepared by dissolving lithium sulfide (1.38 g, 30.2 mmol) in 50 mL of anhyd. methanol (degassed by bubbling argon gas through the liquid with stirring for at least 1 h) in a 100-mL flask. 11-Bromoundecanoic acid (2.00 g, 7.54 mmol) was added and the reaction mixture stirred for 4 h under argon. The reaction was poured, with stirring, into a 500-mL beaker containing diethyl ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a white solid. Recrystallization from hexanes gave white crystals: mp 109-110 °C Further purification was accomplished by flash chromatography using

silica gel and acetone/chloroform (1/3) as eluent, collecting 50-mL fractions. The product was recovered from fractions 5-12 and recrystallized from acetone.

Bis-(16-carbomethoxyhexadecyl)sulfide. Methyl 16-bromohex-adecanoate was prepared from 16-hydroxyhexadecanoic acid as described previously in the procedure for the preparation of 16-hexadecylthiohexadecanoic acid. To a 100-mL round-bottomed flask containing 50 mL of degassed methanol were added methyl 16-bromo-

hexadecanoate (1.0 g, 3.0 mmol) and lithium sulfide (154 mg, 3.1 mmol) and the reaction mixture was stirred under argon overnight at room temperature. The reaction was poured with stirring into a 500-mL beaker containing THF (300 mL). The ethereal layer was extracted with deionized water (2 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation and the residue was recrystallized from hexanes to afford a white solid. Further purification was accomplished by flash chromatography through silica gel using chloroform as the eluent and collecting 50-mL fractions. The product was recovered from fractions 6-10. After removal of the chloroform by rotoevaporation, the product was recrystallized from hexanes to afford white crystals.

Bis-(16-carboxyhexadecyl)sulfide was prepared by the hydrolysis of bis-(16-carbomethoxyhexadecyl)sulfide. The ester was hydrolyzed by refluxing the ester in a solution of THF (100 mL), water (100 mL), and conc. HCl (5 mL) for 4 days. After cooling the

reaction mixture to room temperature, the product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. The solid residue was rinsed with water under suction filtration, dried, and recrystallized from THF, affording a white solid.

Bis-(21-carboxyheneicosyl)sulfide. Ethyl 21-docosenoate was

prepared as described previously[1] from 11-bromoundecene and ethyl 11-iodoundecanoate. The procedure of Brown[2] was followed using ethyl 21-docosenoate (10.0 g, 27.3 mmol) and 1.0 M borane in THF (10 mL, 10.0 mmol, Aldrich). Subsequently, 1 M sodium hydroxide (30.3 mL, 30.3 mmol) and 30% H_2O_2 (10.4 mL, 30.3 mmol) were added to the borane. The THF layer of the reaction mixture was washed with sat. aq. NaCl (3 X 100 mL) dried over anhydrous Na_2SO_4, and filtered. The solvent was removed by rotoevaporation to afford 8.4 g (80% yield) of white solid. ^1H NMR (CDCl$_3$) δ 4.11 (Q, 2 H), 3.63 (t, 2 H), 2.27 (t, 2 H); 1.59 (m); 1.27 (m). Ethyl 22-tosyldocosanoate was prepared following a procedure described previously[3] by adding ethyl 22-hydroxydocosanoate (8.4 g, 21.8 mmol) to a 100-mL round-bottomed flask containing pyridine (60 mL). The solution was warmed until the alcohol dissolved completely and then cooled to 20 °C to form a turbid solution. Tosyl chloride (4.58 g, 24.0 mmol) was added to the flask while keeping the temperature of the mixture below 20 °C. The reaction mixture was allowed to stand in a refrigerator overnight. The crude tosylate was poured into a 1000-mL beaker containing ice-water (400 mL) and conc. HCl (5 mL)

and the mixture was stirred with a spatula. The white precipitate was collected by suction filtration and excess water removed by pressing the product against the Buchner funnel with a spatula. The tosylate was purified further by dissolving it in ether (250 mL) (stirring for several hours at room temperature was necessary), washing the ethereal layer with 0.1 N HCl (100 mL) and with ice-cold deionized water (3 X 100 mL) and drying with anhydrous Na_2SO_4. The ethereal solution was decolorized with Norit, filtered, and the ether removed by rotoevaporation to afford a white solid: mp 67.5-69.6 °C; ^1H NMR $(CDCl_3)$ δ 7.56 (AA'BB', 4 H), 4.12 (Q, 2 H), 4.01 (t, 2 H), 2.44 (s, 3 H), 2.27 (t, 2 H), 1.60 (m, 4 H), 1.24 (m). Ethyl 22-iododocosanoate was prepared as described previously for ethyl 11-iodoundecanoate by dissolving ethyl 22-tosyldocosanoate (3.5 g, 6.51 mmol) and NaI (1.95 g, 13.0 mmol) in 150-mL of acetone in a 250-mL round-bottomed flask and heating the mixture at reflux for 24 h. The reaction mixture was allowed to cool to room temperature and 250 mL of diethyl ether were added to the flask. The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous Na_2SO_4, and filtered. After removal of the ether by rotoevaporation, a white solid was obtained that was purified further by passing through a column of silica gel using ether-hexanes (1/9) as the eluent.

Bis-(21-carboethoxyheneicosyl)sulfide was prepared by adding ethyl 22-iododocosanoate (2.2 g, 4.5 mmol) to 100 mL of degassed, anhydrous methanol in a 250-mL round-bottomed flask.

Lithium sulfide (102 mg, 2.2 mmol) was added and the reaction mixture was heated at reflux under argon overnight. The mixture was cooled to room temperature, filtered and rinsed with deionized water. The white solid was recrystallized from hexanes to afford white crystals of bis-(carboethoxydocosyl)sulfide and bis-(21-carbomethoxyheneicosyl)sulfide. The esters were hydrolyzed in a solution of THF (100 mL), water (100 mL), and conc. HCl (5 mL) for 4 days. The product was isolated by removal of THF by rotoevaporation and filtration of the solid residue using a Buchner funnel. This residue was rinsed with deionized water under suction filtration, dried, and recrystallized from THF, affording a white solid.

Bis-(11-hydroxyundecyl)sulfide was prepared by dissolving lithium sulfide (0.95 g, 20.8 mmol) in 200 mL of degassed anhydr methanol in a 500-mL round-bottomed flask, adding 11-bromo-1-undecanol (5.22 g, 20.8 mmol, 98%, Aldrich, purified by recrystallization from hexanes) and stirring under argon for 24 h. The reaction mixture was poured, with stirring, into a 500-mL beaker containing ether (300 mL). The ethereal layer was extracted with deionized water (3 X 100 mL) and sat. aq. NaCl (100 mL), dried over anhydrous sodium sulfate, and filtered. The ether was removed by rotoevaporation yielding a white solid. Recrystallization from hexanes gave a white solid. Further purification was accomplished by flash chromatography (R_f = 0.4) using silica gel and acetone/chloroform (1/3) as eluent. The product was recrystallized from hexanes.

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1) Bergbreiter, D.E.; Whitesides, G.M. J. Org. Chem. **1975**, 40, 779-782.

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